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(54) Title: DETERGENT COMPOSITIONS COMPRISING A RAW STARCH DEGRADING ENZYME

(57) Abstract: The present invention relates to detergent compositions, including laundry, dishwashing, and/or hard surface cleaner compositions, comprising a raw starch degrading enzyme characterised by a ratio of activity to degrade raw corn starch (Ra) to activity to degrade gelatinised starch (Ga): [Ra/Ga] above 0.2, preferably above 0.35. Such compositions provide excellent removal of starch-containing stains and soils, and when formulated as laundry compositions, excellent whiteness maintenance and dingy cleaning.

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DETERGENT COMPOSITIONS COMPRISING A RAW STARCH DEGRADING ENZYME

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Field of the Invention

The present invention relates to detergent compositions comprising a raw starch degrading enzyme.

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Background of the invention

Performance of a detergent product is judged by a number of factors, including the ability to remove soils. Therefore, detergent components such as surfactants, bleaching agents and enzymes, have been incorporated in detergents. One of such specific example is the use of proteases, lipases, amylases and/or cellulases.

Proteases are commonly used enzymes in cleaning applications. Proteases are known for their ability to hydrolyse other proteins. This ability has been taken advantage of through the incorporation of naturally occurring or engineered protease enzymes in laundry detergent compositions. The inclusion of lipolytic enzymes in detergent compositions for improved cleaning performance is known, e.g. enhancement of removal of triglycerides containing soils and stains from the fabrics. The activity of cellulase is one in which cellulosic fibres or substrates are attacked by the cellulase and is depending on the particular function of the cellulase, which can be endo- or exo- cellulase, and on the respective hemicellulases. The cellulose structures are depolymerized or cleaved into smaller and thereby more soluble or dispersible fractions. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and generally improved handfeel characteristics to the fabric structure. Amylase enzymes have long been recognised in detergent compositions to provide the removal of starchy food residues or starchy films from dishware or hard surfaces or to provide cleaning performance on starchy soils as well as other soils typically encountered in laundry and dishwashing applications.

Indeed, starchy materials such as amylose and amylopectin, constitute one of the major components of the soils /stains encountered in laundry, dishwashing or hard surfaces cleaning operations. Moreover, the textile industry uses starchy materials in their textile finishing processes. Therefore, amylase enzymes have been since a long time incorporated into the detergent products for the removal of starch-containing stains. However, it has been surprisingly found that such commonly used detergent amylases could not hydrolyse raw starch materials effectively.

A substantial part of starch material remains indeed under the raw form even when processed within the food or textile industries. In particular, it has been found that food stains such as rice, spaghettis, potatoes, corn, cereals, etc retrieved on fabric, dishware and other hard surfaces contain a substantial amount of raw starch. Furthermore, it has been surprisingly found that such raw starch remaining on the surfaces, entraps further dirt, and when found on a fabric surface, leads to a dingy appearance of the surface to be cleaned.

As can be seen from the above, there is a need to formulate detergent products which address the removal of such raw starch containing soils/stains. Accordingly, the above objective has been met by formulating a detergent composition comprising an enzyme highly efficient to degrade raw starch. Such enzymes are characterised by a ratio of activity to degrade raw corn starch (Ra) to activity to degrade gelatinised starch (Ga) : [Ra/Ga] above 0.2, preferably above 0.35.

It has been further found that the performance of the detergent compositions of the present invention is enhanced by the addition of a further enzyme selected from a lipase, a protease, an α -amylase and/or a pullulanase (a neopullulanase, a pullulanase type I or II) and/or by the addition of a detergent ingredient selected from nonionic surfactants and/or flocculating agents.

EP 368 341 describes detergent compositions comprising a surfactant and at least one starch debranching enzyme selected from the group consisting of pullulanase, isopullulanase and isoamylase and preferably with an α -amylase for improved starchy dirt detergent. GB 2 228 945 discloses an automatic dishwashing composition comprising an enzyme capable of breaking α -1,6-

glucosidic linkages. WO98/26078 is directed to H mutant α -amylase enzymes
with improved stability. EP 450 627 describes a novel detergent composition
containing an alkaline pullulanase with excellent detergency against starchy soils.
WO94/19468 relates to a DNA fragment containing a gene for alkaline
pullulanase useful as a component of detergents. US 5,665,585 is directed to an
5 amino acid and DNA sequence of a unique glucoamylase P that has a high
debranching activity, a *Trichoderma* host cell transformed with such sequences,
the expression of such recombinant glucoamylase P and the industrial uses in
particular the alcohol fermentation, for the recombinant enzymes and host
10 transformed therewith. US 3,640,877 describes detergent preparation containing
a system of glucose and glucose oxidase or starch, amyloglucosidase and
glucose oxidase as precursor of hydrogen peroxide and a hydroxylamine which
stabilises the hydrogen peroxide formed during the use of the detergent.
WO95/29996 discloses a novel glucose oxidase, a process for its production and
15 its use in bleaching and detergent compositions as well as its use as a dough
strengthenener. Said enzyme has many applications in the personal care area and
the baking industry, preferably in combination with another enzyme selected from
amyloglucosidase, lactoperoxidase, α -amylase or a maltogenic exo-amylase.

20 However, the use of an enzyme highly efficient in the degradation of raw starch,
i.e. an enzyme characterised by a Ra/Ga higher than 0.2, for the removal of raw
starch-containing stains-soils in a detergent composition, has never been
previously recognised.

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Summary of the invention

The present invention relates to detergent compositions, including laundry,
dishwashing, and/or hard surface cleaner compositions, comprising a raw starch
degrading enzyme characterised by a ratio of activity to degrade raw corn starch
30 (Ra) to activity to degrade gelatinised corn starch (Ga) : [Ra/Ga] above 0.2,
preferably above 0.35. Such compositions provide excellent removal of starch-
containing stains and soils, and when formulated as laundry compositions,
excellent whiteness maintenance and dingy cleaning.

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Detailed description of the invention

The essential component of the detergent compositions of the present invention is a raw starch degrading enzyme characterised by a ratio of activity to degrade raw corn starch (Ra) to activity to degrade gelatinised corn starch (Ga) : [Ra/Ga] above 0.2, preferably above 0.35. The enzymes of the present invention are selected within enzymes having an activity on α -branched polysaccharides, more specifically starch substrates, on gelatinised starch.

The ratio of activity to degrade raw corn starch [Ra] to the activity to degrade gelatinised corn starch [Ga] is defined as follows.

The activity of the enzyme, degrading α -branched polysaccharides, more specifically starch substrates, on gelatinised or raw starch, is measured using standard assays to measure enzyme activities. The raw starch degrading index is the ratio of the activities of the tested enzyme on raw starch and on gelatinised starch. The same assay conditions of temperature, pH, ionic strength, buffer, and enzyme concentration are to be used in both assays on gelatinized and raw starches.

The test protocol to obtain the Ra/Ga value of the enzymes is as follows :

- 1) The assays are performed at a temperature of 40°C.
- 2) First, the pH profile of the enzyme is obtained on raw starch. Said profile is conventionally obtained from the plotting of the % activity versus the pH. This optimum pH value will be used for the following enzymes assays.
- 3) The activity of the tested enzyme on gelatinized starch is then determined at said optimum pH.
- 4) The type of starch used is corn starch from Amylum, as being representative of the starch commonly encountered in laundry. A 2% solution of raw starch is used. To obtain the gelatinized starch solution a solution of raw starch is heated to 70°C for at least 60 minutes.
- 5) The composition of the buffer used in the assay depends on the pH optimum of the enzyme. The buffer composition and concentration must be identical for both the raw and gelatinized starch activity measurements.

For examples : for the amyloglucosidase from *Rhizopus*, a 0.1M acetate buffer at pH of 5.0 is used; for the raw starch degrading alkaline

amylase of *Bacillus* sp. IMD 370, a 0.1M Tris maleate buffer at pH 8.0 is used (See 2)).

- 6) The enzyme concentration used in the assay must be identical for both the raw and gelatinized starch activity measurements.
 - 5 7) The enzyme activity is measured by determination of the reducing sugars in solution. Suitable methods are the following : The method of Bernfield for determining reducing sugars using dinitrosalicylic acid is described in Bernfield P., Amylase α and β , Methods Enzymology 1, 149-158 (1955) and the method for determining reducing sugars with copper-bicinchoninate as described in Fox J. D. et al Analytical Biochemistry 195, 93-96 (1991) or in
10 Waffenschmidt S. et al Anal. Biochem. 165, 337-340 (1987). Prior to the determination of reducing sugars, the solutions are boiled for 3 minutes and centrifugated to inactivate the enzyme.
 - 8) The time for incubation to measure the enzyme activities is 6 hours.
 - 15 9) The enzyme activity is expressed as the number reducing sugars produced per hour and per mg of pure active enzyme.
 - 10) The raw starch degrading index is defined as the ratio of the enzyme activity, as obtained in 9), on raw starch and gelatinized starch
- 20 For example, the glucoamylase activity on gelatinised starch is measured, by measuring the release of glucose produced by the enzyme on a 2% gelatinized corn starch reaction mixture. The activity is measured by the release of reducing sugars produced in μmol per hour per mg of pure active enzyme. The same assay can then be used to measure the activity of the enzyme on raw starch, but
25 substituting the 2% gelatinised corn starch by 2% of raw corn starch. In both assays, the temperature is 40C, the same pH and buffer solution is used and the incubation time is 6 hours.

Such raw starch degrading enzyme is generally comprised in the detergent
30 compositions of the present invention at a level of from 0.0002% to 10%, preferably 0.001% to 2 %, more preferably 0.001% to 1% pure enzyme by weight of the total detergent composition.

Suitable raw starch degrading enzymes having [Ra/Ga] above 0.2 for the
35 purpose of the present invention can be selected from the following enzymes classes (IUPAC Classification) : amyloglucosidase EC 3.2.1.3, α -amylase EC

3.2.1.1, beta-amylases EC 3.2.1.2, isoamylase EC 3.2.1.68, pullulanase type I EC 3.2.1.41, isopullulanase EC 3.2.1.57, neopullulanase EC 3.2.1.135, pullulanase type II, dextrin dextranase EC 2.4.1.24, cyclodextrin glycosyltransferase EC 2.4.1.19 and maltogenic alpha-amylase EC 3.2.1.133.

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Preferably, the detergent compositions of the present invention will comprise a combination of several starch degrading enzymes.

10 Suitable for the purpose of the present invention is an amyloglucosidase of the IUPAC Classification EC 3.2.1.3. Such amyloglucosidase is a glucan 1,4- α -glucosidase; is also referred to as "glucoamylase, γ -amylase, lysosomal α -glucosidase, acid maltase or exo-1,4- α -glucosidase" and its systematic name is 1,4- α -D-glucan glucohydrolase. Amyloglucosidases hydrolyse both α -1,4 and α -1,6 linkages in polysaccharides such as starch, liberating glucose units from non-
15 reducing ends of polysaccharides. These two activities are distinct. By hydrolysing α -1,4 and α -1,6 glucosidic bonds, amyloglucosidases liberate β -D-glucose units from terminal non-reducing ends of a glucose polymer such as starch.

Suitable Amyloglucosidases for the purpose of the present invention are
20 Glucoamylase I (GAI) of *Aspergillus awamori* var. kawachi expressed in *Saccharomyces cerevisiae*; Glucoamylase from *Aspergillus awamori* var. x100; Glucoamylase from *Corticium rolfsii*; Glucoamylase GA1 and GA2 with MW of 74 and 96 kDa from *Aspergillus niger*; Glucoamylase from *Rhizoctania solani*; Glucoamylase from *Chalara paradoxa*; Glucoamylase from *Aspergillus shirousami* (Gaase) 68 kDa.; *Aspergillus* sp. K-27 glucoamylase with MW of kDa
25 76 kDa and proteolysis product kDa 48 kDa; Glucoamylase from *Rhizopus* sp. Gluc1 74 kDa; Glucoamylase from *Clostridium thermohydrosulfuricum* and Glucoamylase from *Rhizopus niveus*.

Most preferred glucoamylases are *Aspergillus* sp. K-27 glucoamylase with MW of
30 kDa 76 kDa; Glucoamylase from *Rhizopus niveus*.

Alpha-amylase, EC 3.2.1.1, is a 1,4- α -D-glucan glucohydrolase gives endohydrolysis of 1,4- α -D-glucosidic linkages in polysaccharides containing three or more α -1,45 linked D-glucose units.

35 Suitable alpha-amylases for the purpose of the present invention are α -amylase from *Cryptococcus* sp. S-2 MW 66 kDa.; α -amylase from *Lipomyces*

kononenkoae expressed in *Saccharomyces cerevisiae* 76 kDa; α -amylase from *Bacillus circulans* F-2 expressed in *E. coli* (RSDA); α -amylase from *Aspergillus* sp. K-27; α -amylase from *Bacillus* sp. IMD 434, IMD 370; α -amylase from *Cytophaga* sp.

- 5 Preferred alpha-amylases are α -amylase from *Lipomyces kononenkoae* expressed in *Saccharomyces cerevisiae* 76 kDa

Beta-amylase, EC 3.2.1.2, is a 1,4- α -D-glucan maltohydrolase, provides exohydrolysis of 1,4- α -D-glucosidic linkages in polysaccharides to remove successive maltose units from non-reducing ends of the chain.

10 Suitable β -amylases for the purpose of the present invention are β -amylase from *Emericella nidulans* (*Aspergillus*); β -amylase from *B. substitute* R2 and expressed in *E. coli* and β -amylase from *Clostridium thermosulfurogenes* produced in *Bacillus brevis*.

15 Pullulanase type I enzymes are classified under the IUPAC classification EC 3.2.1.41 and the systematic name α -Dextrin 6-glucanohydrolase. Pullulanase enzymes hydrolyses the 1,6- α -D-glucosidic linkages in pullulan, amylopectin and glycogens and in the α - and β -amylase limit dextrins of amylopectin and glycogen as well as against branched oligosaccharides produced by their partial decomposition. Because of this characteristic, pullulanase is called a "debranching enzyme". Indeed, pullulanase is an enzyme which breaks only α -1,6-glycosidic linkage of pullulan and finally produces maltotriose.

25 Isopullulanase enzymes are classified under the IUPAC classification EC 3.2.1.57 and the systematic name Pullulan 4-glucanohydrolase. The isopullulanase enzymes hydrolyse pullulan to isopanose (6- α -maltosylglucose).

30 Isoamylase enzymes have the ability to debranch glycogen. These are classified under the IUPAC classification EC 3.2.1.68 and the systematic name glycogen 6-glucanohydrolase. The isoamylase enzymes hydrolyse the 1,6- α -D-glucosidic branch linkages in glycogen, amylopectin and their β -limit dextrins. The isoamylases are distinguished from the pullulanase enzyme by their inability to attack pullulan, by limited action on α -limit dextrins and by their complete action on glycogen.

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- Neopullulanase enzymes are defined as enzymes that degrade pullulan to form panose and these are classified under the IUPAC classification EC 3.2.1.135. Neopullulanase enzyme, which is pullulan 4-D-glucanohydrolase, have an ability to cleave both 1,4- and 1,6- glucosidic bonds found in common starch and carbohydrate type stains or soils. For example, this enzyme hydrolyzes pullulan to panose (6- α -D-glucosylmaltose). Specifically, the neopullulanase enzyme can catalyze four types of reactions including the hydrolysis of α -(1 \rightarrow 4)-glucosidic bond, the hydrolysis of α -(1 \rightarrow 6)-glucosidic bond, the transglycosylation to form α -(1 \rightarrow 4)-glucosidic bond, and the transglycosylation to form α -(1 \rightarrow 6)-glucosidic bond. In contrast, other known enzymes catalyze only one of these reactions or if two reactions are catalysed, the second is weak. Also, the four types of reactions are catalyzed by the same mechanism.
- Pullulanase type II enzymes are defined as amylopullulanases and hydrolyzes randomly the α ,1-4 linkages in addition to the branching points (α -1,6-linkages) in polysaccharides and dextrans, in contrast to pullulanase type I enzymes which only hydrolyze α ,1-6 linkages in branched polysaccharides.
- A further suitable enzyme from the amylase class, is the dextrin dextranase. Dextrin dextranase (EC 2.4.1.2) is an enzyme that produces Dextran and low molecular weight oligosaccharides from starch.
- Cyclomaltodextrin glucanotransferase, EC 2.4.1.19, is an enzyme that cyclizes part of a 1,4- α -D-glucan chain by formation of a 1,4- α -D-glucosidic bond and has the systematic name of 1,4- α -D-glucan 4- α -D-(1,4- α -D-glucano)-transferase (cyclizing).
- Suitable enzymes for the purpose of the present invention are CGT-ase from *Bacillus circulans* 251; CGT-ase from *Bacillus circulans* E192; CGT-ase from *Bacillus* sp. B1018 and CGT-ase from *Bacillus firmus*.

Maltogenic alpha-amylase

- Also suitable is a maltogenic alpha amylase of the IUPAC Classification EC 3.2.1.133 that hydrolyses 1,4- α -D-glucosidic linkages in polysaccharides so as to remove successive alpha-maltose units from the nonreducing ends of the chains. Suitable maltogenic alpha-amylases are the amylase cloned from *Bacillus* as

described in EP 120 693 commercially available under the tradename Novamyl from Novo Nordisk A/S; the variants of maltogenic alpha-amylase having CGT-ase activity and variants of CGT-ase having maltogenic alpha-amylase activity, as well as constructed hybrid enzymes described in WO99/43793 and the maltogenic
5 alpha-amylases variants with improved properties (altered physicochemical properties., e.g. an altered pH optimum, improved thermostability, increased specific activity, an altered cleavage pattern or an increased ability to reduce retrogradation of starch or staling of bread), based on the three-dimensional structure of the maltogenic alpha-amylase Novamyl described in WO99/47394.

10 A specific enzyme that fulfils the Ra/Ga criteria of the present invention is for example the amyloglucosidase from *Rhizopus niveaus* sold by Amano under the tradename Gluczyme and the alpha-amylase from *Lipomyces konomenkoae* from LKA1 gene

15 In another embodiment of the present invention, the detergent compositions of the present invention might further comprise one or more starch-binding domain. Such starch binding domain might be added in the detergent compositions of the present invention, as such, or might be part of a chimeric raw starch degrading
20 enzyme hybrid. Indeed, the raw starch degrading enzymes of the present invention will preferably have or will be added a Starch Binding Domain (SBD). In general enzymes such as amylases, cellulases and xylanases have a modular structure consisting of a catalyst domain and at least one non-catalytic domain whose function is generally described as that of a polysaccharide-binding domain
25 (PBD), starch-binding domain (SBD), cellulose-binding domain (CBD) and xylan-binding domain. The function of these binding domains is to bind selectively to the substrate of the enzyme, and in particular, the primary function of SBD is to bind to starch. It has been found surprisingly found that the detergent compositions of the present invention comprising one or more SBD and/or
30 wherein the raw starch degrading enzymes comprise such a SBD will provide a more effective starch-containing soils/stains removal. It has further been found that such enzymes can be formulated in a more cost-effective manner. Without wishing to be bound by theory, it is believed that such raw starch degrading enzymes will be more effectively directed specifically to their substrate from the
35 wash solutions and so have improved deposition onto the starch containing stains/soils for improved and/or new performance. Moreover, it is believed that

the binding of the SBD will disrupt the surface of starch resulting in a higher hydrolytic rate.

Suitable SBD for use in the present invention are the SBDs comprised in the glucoamylase from *Aspergillus niger* (Sigma) and in the β -galactosidase from *A. awamori*. The recovery and fusion of SBDs can be achieved as described in
5 Ford, C. et al., *J. Cell. Biochem. (Suppl.)* 14D:30 (1990) and in Chen, L. et al., *Abst. Annu. Meet. Am. Soc. Microbiol.* 90:269 (1990).

The above-mentioned enzymes may be of any suitable origin, such as vegetable,
10 animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via
15 protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability,
20 catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the
25 substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

The above-mentioned enzymes may be of any suitable origin, such as vegetable,
30 animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via
35 protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly

encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

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In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

15

Detergent components

The detergent compositions of the invention must contain at least one additional detergent component. The precise nature of these additional component, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The detergent compositions of the present invention will preferably comprise a further enzyme selected from a protease, a lipase, a conventional α -amylase, a conventional neopullulanase, a conventional pullulanase type I or II; a flocculating agent and/or a nonionic surfactant.

In a preferred embodiment, the present invention relates to a laundry and/or fabric care composition comprising a raw starch degrading enzyme (Examples 1-16). In a second embodiment, the present invention relates to dishwashing or household cleaning compositions (Examples 17-23).

The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable

for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning operations. When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a
5 surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing
10 method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry
15 compositions can also contain softening agents, as additional detergent components. Such compositions containing an amyloglucosidase provide starch-containing stain removal, whiteness maintenance and dingy cleaning when formulated as laundry detergent compositions.

20 The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the invention can be liquid, paste, gels,
25 bars, tablets, spray, foam, powder or granular. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form. If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C. The "compact" form of the compositions herein is best reflected by density
30 and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total
35 composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the

- present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate. Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.
- Suitable detergent compounds for use herein are selected from the group consisting of the below described compounds.

Surfactant system

- The detergent compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants. Preferably, the detergent compositions of the present invention will comprise a nonionic surfactant, preferably a nonionic surfactant based upon polyoxyethylene condensates with alcohols. Indeed, it has been surprisingly found that the detergent compositions of the present invention further comprising a nonionic surfactant provide improved removal of starch from fabrics, dishware and other hard surfaces. Without wishing to be bound by theory, it is believed that the nonionic surfactant adsorbs onto the granular surface of the starch, thereby disrupting the starch structure and increasing the raw starch degrading enzyme access to its substrate. Hence, the starch-containing stains / soils is more easily hydrolysed by the enzyme and a synergistic breakdown of the starch soil by the raw starch degrading enzyme and the non-ionic surfactant occurs.
- The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accord with the invention.
- The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the

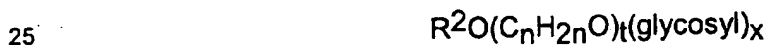
surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Nonionic surfactants : Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM

45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units. The preferred alkylpolyglycosides have the formula



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

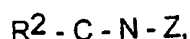
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Other suitable nonionic surfactants are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

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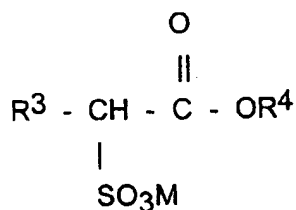




wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or
 5 a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl
 having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to
 the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a
 straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or
 mixtures thereof, and Z is derived from a reducing sugar such as glucose,
 10 fructose, maltose, lactose, in a reductive amination reaction.

Anionic surfactants : Suitable anionic surfactants to be used are linear alkyl
 benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-
 C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃
 15 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp.
 323-329. Suitable starting materials would include natural fatty substances as
 derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications,
 20 comprise alkyl ester sulfonate surfactants of the structural formula :



25 wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof,
 R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is
 a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable
 salt-forming cations include metals such as sodium, potassium, and lithium, and
 30 substituted or unsubstituted ammonium cations, such as monoethanolamine,
 diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is
 methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates
 wherein R³ is C₁₀-C₁₆ alkyl.

35 Other suitable anionic surfactants include the alkyl sulfate surfactants which are
 water soluble salts or acids of the formula ROSO₃M wherein R preferably is a

C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl- ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k-CH_2COO-M^+$ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to

Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about
 5 3% to about 20% by weight of such anionic surfactants.

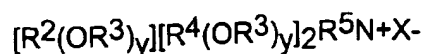
Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl
 10 component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or
 15 substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine,
 20 diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{18}E(2.25)M$), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{18}E(3.0)M$), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and
 25 potassium.

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

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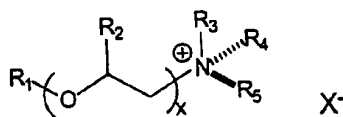
Cationic surfactants : Cationic surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants

35 having the formula :



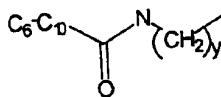
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



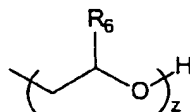
Formula I

whereby R₁ is a short chainlength alkyl (C₆-C₁₀) or alkylamidoalkyl of the formula (II):



Formula II

y is 2-4, preferably 3.
 whereby R₂ is H or a C₁-C₃ alkyl,
 whereby x is 0-4, preferably 0-2, most preferably 0,
 whereby R₃, R₄ and R₅ are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxylated alkyl of the formula III,
 whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R6 is C₁-C₄ and z is 1 or 2.

- 5 Preferred quat ammonium surfactants are those as defined in formula I whereby
 R₁ is C₈, C₁₀ or mixtures thereof, x=0,
 R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

- Highly preferred cationic surfactants are the water-soluble quaternary ammonium
 10 compounds useful in the present composition having the formula :



- wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl,
 C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄O)_xH where x has a value from 2 to 5,
 15 and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

- The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl
 group is a mixture of chain lengths derived from coconut or palm kernel fat or is
 derived synthetically by olefin build up or OXO alcohols synthesis. Preferred
 groups for R₂R₃ and R₄ are methyl and hydroxyethyl groups and the anion X
 20 may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use
 herein are :

- coconut trimethyl ammonium chloride or bromide;
- coconut methyl dihydroxyethyl ammonium chloride or bromide;
- 25 decyl triethyl ammonium chloride;
- decyl dimethyl hydroxyethyl ammonium chloride or bromide;
- C₁₂-15 dimethyl hydroxyethyl ammonium chloride or bromide;
- coconut dimethyl hydroxyethyl ammonium chloride or bromide;
- myristyl trimethyl ammonium methyl sulphate;
- 30 lauryl dimethyl benzyl ammonium chloride or bromide;
- lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
- choline esters (compounds of formula (i) wherein R₁ is
 CH₂-CH₂-O-C-C₁₂-14 alkyl and R₂R₃R₄ are methyl).

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di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent
5 4,228,044, Cambre, issued October 14, 1980 and in European Patent
Application EP 000,224.

Typical cationic fabric softening components include the water-insoluble
quaternary-ammonium fabric softening actives or their corresponding amine
10 precursor, the most commonly used having been di-long alkyl chain ammonium
chloride or methyl sulfate.

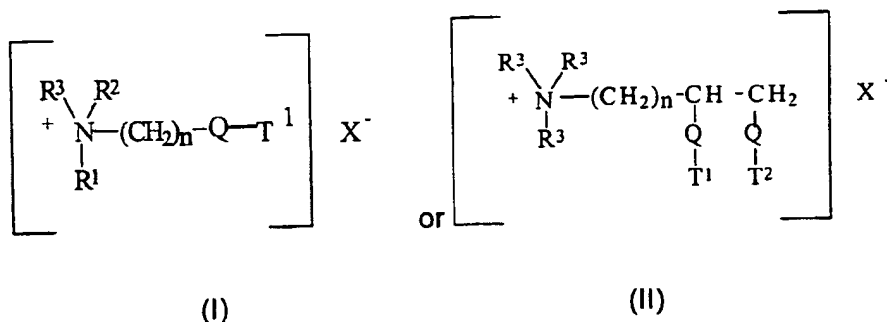
Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 15 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 20 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
- 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 25 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as
30 alternatives to the traditionally used di-long alkyl chain ammonium chlorides and
methyl sulfates. Such quaternary ammonium compounds contain long chain
alk(en)yl groups interrupted by functional groups such as carboxy groups. Said
materials and fabric softening compositions containing them are disclosed in
numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

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The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

- 10 R¹ is (CH₂)_n-Q-T² or T³;
 R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;
 R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;
 R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;
 T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;
 15 n and m are integers from 1 to 4; and
 X⁻ is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

20 The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

25 Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 30 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;

- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
 - 5 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
 - 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

- 10 When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

15 Ampholytic surfactants : Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to

20 about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention

25 typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants : Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as

30 derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

- 5 Semi-polar nonionic surfactants : Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble
10 phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and
15 hydroxyalkyl moieties of from about 1 to about 3 carbon atoms. Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

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↑



- wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl
25 group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

- These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl
30 amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

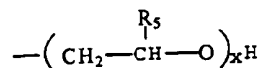
When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

- 35 Co-surfactants : The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain or $R_4X(CH_2)_n$, X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C_8 - C_{10} oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

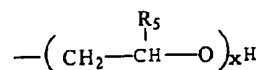
Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R_1 and R_2 are C_1 - C_8 alkylchains or



R_3 is either a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain, or R_3 is $R_4X(CH_2)_n$, whereby X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_4 - C_{12} , n is between 1 to 5, preferably 2-3. R_5 is H or C_1 - C_2 alkyl and x is between 1 to 6.

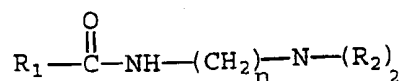
R_3 and R_4 may be linear or branched; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $R_1R_2R_3N$ where R_1 is a C_6 - C_{12} alkyl chain, R_2 and R_3 are C_1 - C_3 alkyl or



where R_5 is H or CH_3 and $x = 1-2$.

Also preferred are the amidoamines of the formula:



wherein R_1 is C_6 - C_{12} alkyl; n is 2-4,

preferably n is 3; R_2 and R_3 is C_1 - C_4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyl dimethylamine, C8-10 amidopropyl dimethylamine and C10 amidopropyl dimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyl dimethylamine and bis(hydroxyethyl)coconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Conventional detergent enzymes

The detergent compositions can in addition to the raw starch degrading enzyme, further comprise one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, mannanases, xyloglucanases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipooxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

Preferably, the detergent compositions of the present invention will comprise a enzyme selected from a protease, a lipase, a conventional α -amylase, a conventional neopullulanase and/or a conventional pullulanase type I or II. By conventional it is meant, an amylase or a pullulanase which does not fall within the Ra/Ga ratio as defined in the present invention.

Indeed, it has been found that the combination of a raw starch degrading enzyme with an enzyme from the amylase class, i.e. a conventional α -amylase, a conventional neopullulanase and/or a conventional pullulanases type I or II, within the detergent compositions of the present invention, provides a synergistic removal of raw starch. Hence, the detergent compositions comprising such

combination of enzyme provide enhanced removal of starch-containing stains and soils and when formulated as a laundry detergent composition, enhanced whiteness maintenance and dingy cleaning.

- 5 Furthermore, the stains most commonly encountered in laundry, dishwashing and hard surface cleaning, generally comprise a significant amount of proteins and triglyceride compounds. In particular, it has been found that starch materials are usually associated with lipid compounds. Therefore, the detergent compositions will preferably comprise a protease and/or lipase enzyme in order
10 to enhance the removal of such complex stains.

Alpha-amylase

- As indicated above, the detergent compositions of the present invention will preferably comprise an α -amylase. Suitable α -amylases for the purpose of the
15 present invention are described in the following : WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include
20 those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants
25 having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk). Examples of commercial α -amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban®, Fungamyl® and Duramyl®, all available
30 from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay. Preferred are variants of the above enzymes, described
35 in WO96/23873 (Novo Nordisk). Preferably, the variants are those demonstrating improved thermal stability, more preferably those wherein at least one amino acid

residue equivalent to F180, R181, G182, T183, G184, or K185 has been deleted from the parent α -amylase. Particularly preferred are those variants having improved thermal stability which comprise the amino acid deletions R181 + G182 or T183 + G184. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermal stability and a higher activity level are described in WO95/35382. Further suitable amylases are the H mutant α -amylase enzymes exhibiting improved stability described in WO98/26078 by Genencor.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

Pullulanase type I

Pullulanase type I is a starch debranching enzymes and can be obtained from various sources. Generally, however, it is derived from microorganisms. Pullulanase type I is generally comprised in the detergent composition of the invention in an amount of 0.0001% to 10% by weight, preferably 0.001% to 0.5% by weight.

Pullulanase type I enzymes are classified under the IUPAC classification EC 3.2.1.41 and the systematic name α -Dextrin 6-glucanohydrolase. Pullulanase enzymes hydrolyses the 1,6- α -D-glucosidic linkages in pullulan, amylopectin and glycogens and in the α - and β -amylase limit dextrins of amylopectin and glycogen as well as against branched oligosaccharides produced by their partial decomposition. Because of this characteristic, pullulanase is called a "debranching enzyme". Indeed, pullulanase is an enzyme which breaks only α -1,6-glycosidic linkage of pullulan and finally produces maltotriose.

Microbial sources include *Aerobacter Aerogenes*, *Pseudomonas, stutzeri*, *Bacillus polymyxa*, *B.maceranas*, *Klebsiella pneumonia* and *Streptomyces* sp. The activity of this enzyme is standardised at 200 PUN/g (Pullulanase Unit Novo). 1UPN is defined as the amount of enzyme which under standard conditions hydrolyses pullulan liberating reduced carbohydrate, with a reducing power equivalent to 1 μ -mole glucose per minute. The enzyme is stable at below 60°. Also preferred is pullulanase isolated from a strain of *Bacillus* No. 202-1 as described in *Biochimica et Biophysica Acta*, 397 (1985) 188-193. This

pullulanase has an optimum pH of about 8.55-9.0, and is therefore of particular interest in more alkaline detergent compositions.

Pullulanase was first discovered from a strain belonging to *Aerobacter aerogenes* by Bender and Wallenfels in 1961 [*Biochem. Z.*, 334, 79, (1961)]. Recently, various microorganisms capable of producing pullulanase have been reported. These microorganisms are, for example, *Bacillus* sp. [*J. Jpn. Soc. Starch Sci.*, 30, 200, (1983)]; *Bacillus acidopullulyticus* [*Agric. Biol. Chem.*, 52, 2293, (1984)]; *Bacillus stearothermophilus* [*Eur. J. Appl. Microbiol. Biotechnol.*, 17, 24, (1983)]; *Streptococcus mitis* - [*Biochem. J.*, 108, 33, (1968)]; *Lactobacillus* [Denpun Kagaku, 28, 72 (1981)]; *Clostridium* sp. [*Appl., Environ. Microb.*, 53, 7 (1987)]; *Clostridium thermohydrosulfuricum* [*Appl. Environ. Microb.*, 49, 5, (1985), *J. Bacteriol.*, 164, 3, (1985), *Biochem. J.*, 246, (1987)], *Thermus aquaticus* [*Enzyme Microb. Technol.*, 8, (1986)]; *Thermus* sp. [*J. Jpn. Soc. Starch Sci.*, 34, 1, (1987)] and *Clostridium thermosulfurogenes* [*Appl. Microb. Biotechnol.*, 33, 511, (1990)]. Furthermore, two publications have reported a method of producing alkaline or alkaline-resistant pullulanases: Horikoshi et al. cultured an alkalophilic strain of the genus *Bacillus* (*Bacillus* sp. 202-1) and produced alkaline pullulanase (Japanese Patent Publication (Kokoku) No. 277786/1978); and the alkaline pullulanase from *Bacillus* sp. KSM-AP 1876 described in WO94/19468 (Japanese Patent Application Laid-open (Kokai) No. 87176/1991). Relevant pullulanase include for example, pullulanases obtainable from *Bacillus* species (e.g. *B. acidopullulyticus* as described in EP 063 909, such as PromozymeTM from Novo Nordisk A/S). Further pullulanase suitable for the detergent compositions of the present invention is the alkaline pullulanase described in EP 450 627 by the Kao Corporation, which has an optimum pH in the alkaline range and is stable against surfactants. Such alkaline pullulanase includes an alkaline pullulanase A and an alkaline pullulanase B, both suitable for the purpose of the present invention. Another alkaline pullulanase suitable for detergents is described in WO94/19468 by the Kao Corporation. Also suitable are the pullulanase enzymes described in the following Japanese patent/applications : JP04073298 which is directed to an automatic dishwashing detergent composition comprising a nonionic surfactant, a calcium chelating agent, a lipase and an alkali pullulanase for high detergency, JP06264094 which describes a laundry detergent composition comprising soaps, surfactants and alkali-resistant pullulanase having high detergency; all by the Kao Corporation.

Particularly preferred is the Pullulanase Promozyme (Trade Mark of Novo), isolated from *Bacillus* sp. Pullulanase.

Also suitable are the pullulanase enzymes described as starch debranching enzymes in the following Japanese patent/applications : JP 07179900, JP06172796, JP06172792, JP04065494, JP02132193 and JP 02132192, all by
5 the Kao Corporation.

Neopullulanase

A further suitable enzyme from the amylase class is Neopullulanase.
10 Neopullulanase enzymes are defined as enzymes that degrade pullulan to form panose and these are classified under the IUPAC classification EC 3.2.1.135. Neopullulanase enzyme, which is pullulan 4-D-glucanohydrolase, have an ability to cleave both 1,4- and 1,6- glucosidic bonds found in common starch and carbohydrate type stains or soils. For example, this enzyme hydrolyzes pullulan
15 to panose (6- α -D-glucosylmaltose). Specifically, the neopullulanase enzyme can catalyze four types of reactions including the hydrolysis of α -(1 \rightarrow 4)-glucosidic bond, the hydrolysis of α -(1 \rightarrow 6)-glucosidic bond, the transglycosylation to form α -(1 \rightarrow 4)-glucosidic bond, and the transglycosylation to form α -(1 \rightarrow 6)-glucosidic bond. In contrast, other known
20 enzymes catalyze only one of these reactions or if two reactions are catalysed, the second is weak. Also, the four types of reactions are catalyzed by the same mechanism. Neopullulanase enzymes are described in the following publications: Enzyme Chemistry and Molecular Biology of Amylases and Related Enzyme, pages 28-32 (1995), edited by the Amylases research Society of Japan; H.
25 Takata, et al. J. Biol. Chem., volume 267, number 26, pages 15447-15452 (1992).

Neopullulanase enzyme can be produced by the so called wild-type organism or by any host organism in which the gene responsible for the production of the neopullulanase, has been cloned and expressed. For example, the enzyme can
30 be isolated from the culture supernatant of *Bacillus stearothermophilus* (*B. stearothermophilus*) TRS40 and purified to homogeneity using sodium dodecyl sulfate-polyacrylamide gel electrophoresis. Another enzyme having a molecular weight of 62,000 was cloned and expressed in *Bacillus subtilis*. This type of enzyme is fairly thermostable, particularly at an optimum temperature of from
35 60°C to 65°C at pH 6, and about 90% of the enzyme activity is retained. *Bacteroides thetaiotaomicron* 95-1 (*B. thetaiotaomicron* 95-1) is another type of

enzyme, found in the human colon in high numbers. *B. thetaiotaomicron* 95-1 can ferment a wide variety of polysaccharides.

Also suitable neopullulanase for use in the present invention is the new neopullulanase Y377F, S422V or M375L which is originated from *Bacillus*
5 *staerothermophilus* as described in JP07177891; is the neopullulanase from *B. subtilis* as described in JP06121681; is the neopullulanase from *Bacillus stearothermophilus* TRS (FERM9690), *Thermoactinomyces vulgaris*, *Bacillus stearothermophilus* KP1064, *Bacteroides thetaiotaomicron* 95-1 and others as described in JP05316992; is the variation-type neopullulanase described in
10 JP04020291 and the neopullulanase described in JP02276578.

The neopullulanase is generally comprised in the detergent composition of the invention in an amount of 0.0001% to 10% by weight, preferably 0.001% to 0.5% by weight.

15 Pullulanase type II

Pullulanase type II enzymes are defined as amylopullulanases and hydrolyzes randomly the α ,1-4 linkages in addition to the branching points (α -1,6-linkages) in polysaccharides and dextrans, in contrast to pullulanase type I enzymes which only hydrolyse α ,1-6 linkages in branched polysaccharides.

20 The pullulanase type II can originate from extremophiles, especially extreme thermophiles and hyperthermophiles such as those isolated from *Pyrococcus woesei*, *P. furiosus*, *Thermococcus litoralis*, *Thermococcus celer*, *Desulfurococcus mucosus*, *Bacteroides thetaiotaomicron*, *Staphylothermus marinus*, *Pyrodictium abyssii*, *Bacillus stearothermophilus* such as described in "A
25 new Bacterial World", Extremophiles, 1997, 1:2-13. Other suitable pullulanase for the purpose of the present invention is the alkaline pullulanase exhibiting alkaline α -amylase activity described in WO 96/35794. Also suitable is the alkaline pullulanase Y having an α -amylase activity as described in EP 418 835, having an optimum pH at higher alkaline range than conventional alkaline pullulanases
30 and exhibiting excellent pH stability in a wide pH range and strong resistance to almost all detergent ingredients such as surfactants, chelating agents and proteases.

Also suitable is a combined enzyme of pullulanase-amylase produced by *Bacillus subtilis* TU (*Agric. Biol. Chem.*, 51, 9. (1987); Japanese Patent Publication No.
35 18717/1989).

The pullulanase type II is generally comprised in the detergent composition of the invention in an amount of 0.0001% to 10% by weight, preferably 0.001% to 0.5% by weight.

5 Suitable lipase enzymes include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from
10 Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp.,
15 U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258
20 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-
25 88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

30

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of
35 Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include

ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in WO 91/06637. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and WO95/10592. The "protease D" variants have preferably the amino acid substitution set 76/103/104, more preferably the substitution set N76D/S103A/V104I. Also suitable is a carbonyl hydrolase variant of the protease

described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application published under WO98/55634).

More preferred proteases are multiply-substituted protease variants. These protease variants comprise a substitution of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company. Preferred multiply substituted protease variants have the amino acid substitution set 101/103/104/159/232/236/245/248/252, more preferably

101G/103A/104I/159D/232V/236H/245R/248D/252K according to the numbering of *Bacillus amyloliquefaciens subtilisin*.

The protease enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

The detergent compositions of the present invention can further comprise other enzymes :

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point
5 may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in
10 these domains.

The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

15 Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

20 A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place
25 et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme
30 stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

35 ***Bleaching agent***

A further suitable ingredient of the detergent compositions of the present invention include bleaching agents. Suitable bleaching agents for the purpose of the present invention include hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can
5 include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

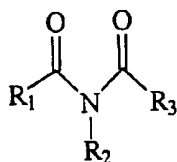
10 The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

15 One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents
20 are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the
25 halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

30 The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylenethylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or
35 pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are

perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7 and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



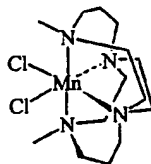
wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl group.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3. The bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the

art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})\text{-}(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. More preferred for use therein are the transition -metal bleach catalysts being complexes of a transition metal and a cross bridged macropolycyclic ligands such as described in Procter & Gamble patent applications WO 98/39405, WO 98/39406 and WO 98/39098. Most preferred is the Mn Complex Bleach Catalyst of the formula $[\text{Mn}(\text{Bcyclam})\text{Cl}_2]$ illustrated as:



"Bcyclam" (5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane). Such transition -metal bleach catalyst can be prepared according to Procter & Gamble patent application WO98/39335 or according to J.Amer.Chem.Soc., (1990), 112, 8604.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Colour care and fabric care benefits

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in copending European Patent Application
5 No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer (PCT/US97/16546) for colour care treatment and perfume substantivity are further examples of colour care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

10 Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening
15 agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight
20 polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening
25 agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15%
30 to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

35 **Builder system**

- The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.
- 10 Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP. Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate
- 15 ($\text{Na}_2\text{Si}_2\text{O}_5$). Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy)
- 20 diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates,
- 25 aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.
- 30 Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate
- 35 derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British

Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-
5 tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan
- cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-
tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and
and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol
and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and
10 the phthalic acid derivatives disclosed in British Patent No. 1,425,343.
Of the above, the preferred polycarboxylates are hydroxycarboxylates containing
up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture
15 of a water-insoluble aluminosilicate builder such as zeolite A or of a layered
silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric
acid. Other preferred builder systems include a mixture of a water-insoluble
aluminosilicate builder such as zeolite A, and a watersoluble carboxylate
chelating agent such as citric acid. Preferred builder systems for use in liquid
20 detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in
granular compositions include inorganic materials such as alkali metal
carbonates, bicarbonates, silicates, and organic materials such as the organic
25 phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.
Other suitable water-soluble organic salts are the homo- or co-polymeric acids or
their salts, in which the polycarboxylic acid comprises at least two carboxyl
radicals separated from each other by not more than two carbon atoms.
Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts
30 are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride,
such copolymers having a molecular weight of from 20,000 to 70,000, especially
about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by
35 weight of the composition preferably from 10% to 70% and most usually from
30% to 60% by weight.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron
5 and/or manganese chelating agents. Such chelating agents can be selected from
the group consisting of amino carboxylates, amino phosphonates,
polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as
hereinafter defined. Without intending to be bound by theory, it is believed that
10 the benefit of these materials is due in part to their exceptional ability to remove
iron and manganese ions from washing solutions by formation of soluble
chelates.

Amino carboxylates useful as optional chelating agents include
ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-
15 triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates,
diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium,
and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the
compositions of the invention when at least low levels of total phosphorus are
20 permitted in detergent compositions, and include ethylenediaminetetrakis
(methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates
to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the
compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to
25 Connor et al. Preferred compounds of this type in acid form are
dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate
("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233,
30 November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic
acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for
example, insoluble builders such as zeolites, layered silicates and the like.

35

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

5

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components. A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil®.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

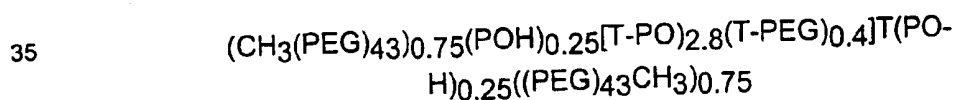
Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-

2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium
 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium
 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene-
 2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-
 5 sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are
 the specific brighteners disclosed in EP 753 567.

The detergent compositions of the present invention will preferably further
 comprise a flocculating agent. Indeed, flocculating agents are known to be able
 10 to flocculate particles. Without wishing to be bound by theory, it is believed that
 these flocculating agents help to prevent raw starch granules to adsorb on the
 fabric surface by keeping them in solution and flocculating them together. This will
 prevent large amounts of starch to deposit on the fabric surface and the raw
 starch degrading enzyme will degrade the raw starch on the fabric surface and
 15 solution. Therefore, the detergent compositions of the present invention further
 comprising a flocculating agent will deliver improved starch-containing stains and
 soil removal and when formulated as a laundry composition, improved whiteness
 maintenance and dingly cleaning benefits.

Suitable flocculating materials are the polyethylene glycols, particularly those of
 20 molecular weight 200-10000, more particularly 2000 to 8000 and most preferably
 about 4000. These are generally used at levels of from 0.20% to 5% more
 preferably from 0.25% to 2.5% by weight. These polymers and the previously
 mentioned homo- or co-polymeric polycarboxylate salts are valuable for
 improving whiteness maintenance, fabric ash deposition, and cleaning
 25 performance on clay, proteinaceous and oxidizable soils in the presence of
 transition metal impurities.

Soil release agents useful in compositions of the present invention are
 conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol
 30 and/or propylene glycol units in various arrangements. Examples of such
 polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and
 4711730 and European Published Patent Application No. 0 272 033. A particular
 preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(OC_2H_4)_nO-$, PO is $(OC_3H_6O)_n$ and T is $(pOC_6H_4CO)_n$.

Also very useful are modified polyesters as random copolymers of dimethyl
5 terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol,
the end groups consisting primarily of sulphobenzoate and secondarily of mono
esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer
capped at both end by sulphobenzoate groups, "primarily", in the present context
most of said copolymers herein will be end-capped by sulphobenzoate groups.
10 However, some copolymers will be less than fully capped, and therefore their end
groups may consist of monoester of ethylene glycol and/or propane 1-2 diol,
thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl
terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight
15 ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about
15% by weight of sulfoisophthalic acid, and have a molecular weight of about
3.000. The polyesters and their method of preparation are described in detail in
EPA 311 342.

20 It is well known in the art that free chlorine in tap water rapidly deactivates the
enzymes comprised in detergent compositions. Therefore, using chlorine
scavenger such as perborate, ammonium sulfate, sodium sulphite or
polyethyleneimine at a level above 0.1% by weight of total composition, in the
formulas will provide improved through the wash stability of the detergent
25 enzymes. Compositions comprising chlorine scavenger are described in the
European patent application 92870018.6 filed January 31, 1992.

Alkoxyated polycarboxylates such as those prepared from polyacrylates are
useful herein to provide additional grease removal performance. Such materials
30 are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated
herein by reference. Chemically, these materials comprise polyacrylates having
one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the
formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-
chains are ester-linked to the polyacrylate "backbone" to provide a "comb"
35 polymer type structure. The molecular weight can vary, but is typically in the

range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Dispersants

5 The detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this
10 type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000. Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can
15 be added in the detergent compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no
20 more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap
25 dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163,
30 (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO₃ (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C₁₆-C₁₈ dimethyl amine oxide, C₁₂-C₁₈ alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C₁₂-C₁₅ alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C₁₄-C₁₅ ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Dye transfer inhibition

The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

Polymeric dye transfer inhibiting agents

The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes

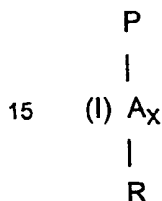
washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

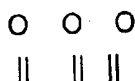
Addition of such polymers also enhances the performance of the enzymes according the invention.

10 a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :



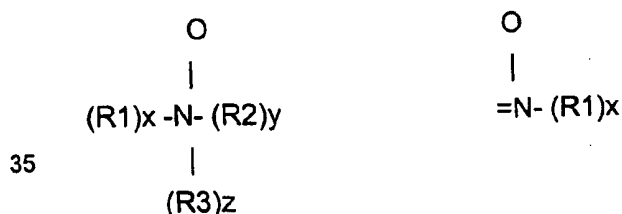
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

30 The N-O group can be represented by the following general structures :



wherein R₁, R₂, and R₃ are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting

properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics, dishware or any other hard surface with a cleaning solution in the usual manner and exemplified hereunder. A conventional laundry method comprises treating soiled fabric with an aqueous liquid having dissolved or dispensed therein an effective amount of the laundry detergent and/or fabric care composition. A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres. According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition. A conventional hard surface method comprises treating soiled hard items with e.g. a sponge, brush, clothe, etc. with an aqueous

liquid having dissolved or dispensed therein an effective amount of the hard surface cleaner and/or with such composition undiluted. It also encompasses or the soaking in a concentrated solution or in a large volume of dilute solution of the detergent composition. The process of the invention is conveniently carried
 5 out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

The following examples are meant to exemplify compositions of the present
 10 invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the
 15 detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

| | |
|--------------------------------|--|
| LAS | : Sodium linear C ₁₁₋₁₃ alkyl benzene sulphonate. |
| TAS | : Sodium tallow alkyl sulphate. |
| C _{xy} AS | : Sodium C _{1x} - C _{1y} alkyl sulfate. |
| C _{xy} SAS | : Sodium C _{1x} - C _{1y} secondary (2,3) alkyl sulfate. |
| C _{xy} Ez | : C _{1x} - C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide. |
| C _{xy} EzS | : C _{1x} - C _{1y} sodium alkyl sulfate condensed with an average of z moles of ethylene oxide. |
| C _x EO _y | : C _y alcohol with an average of ethoxylation of y. |
| Nonionic | : Mixed ethoxylated/propoxylated fatty alcohol e.g. Plurafac LF404 being an alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5. |
| QAS | : R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ -C ₁₄ . |
| QAS 1 | : R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ -C ₁₁ . |
| SADS | : Sodium C ₁₄₋₂₂ alkyl disulphate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄ -) ₂ where R=C ₁₀₋₁₈ |

| | |
|--------------|--|
| MBAS | : C12-18 mid branched alkyl sulphate surfactant with an average branching of 1.5 methyl or ethyl branching groups |
| MES | : x-Sulpho methylester of C18 fatty acid |
| APA | : C8-10 amido propyl dimethyl amine. |
| Soap | : Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids. |
| STS | : Sodium toluene sulphonate. |
| TFAA | : C16-C18 alkyl N-methyl glucamide. |
| TPKFA | : C12-C14 topped whole cut fatty acids. |
| DEQA | : Di-(tallow-oxy-ethyl) dimethyl ammonium chloride. |
| DEQA (2) | : Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate. |
| SDASA | : 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid. |
| DTMAMS | : Ditalow dimethyl ammonium methylsulfate. |
| Silicate | : Amorphous Sodium Silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.6-3.2:1). |
| Metasilicate | : Sodium metasilicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.0). |
| Zeolite A | : Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis). |
| SKS-6 | : Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$. |
| Citrate | : Tri-sodium citrate dihydrate. |
| Citric | : Anhydrous citric acid. |
| Carbonate | : Anhydrous sodium carbonate. |
| Bicarbonate | : Sodium hydrogen carbonate. |
| Sulphate | : Anhydrous sodium sulphate. |
| Mg Sulphate | : Anhydrous magnesium sulfate. |
| STPP | : Sodium tripolyphosphate. |
| TSP | : Tetrasodium pyrophosphate. |
| MA/AA | : Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000. |
| MA/AA 1 | : Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000. |

| | |
|-----------------------|---|
| AA | : Sodium polyacrylate polymer of average molecular weight 4,500. |
| Polycarboxylate | : Copolymer comprising mixture of carboxylated monomers such as acrylate, maleate and methacrylate with a MW ranging between 2,000-80,000 such as Sokolan commercially available from BASF, being a copolymer of acrylic acid, MW4,500. |
| Clay | : Bentonite or smectite clay |
| PB1 | : Anhydrous sodium perborate monohydrate. |
| PB4 | : Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$. |
| Percarbonate | : Anhydrous sodium percarbonate of nominal formula $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$. |
| NaDCC | : Sodium dichloroisocyanurate. |
| TAED | : Tetraacetyl ethylene diamine. |
| NOBS | : Nonanoyloxybenzene sulfonate in the form of the sodium salt. |
| NACA-OBS | : (6-nonamidocaproyl) oxybenzene sulfonate. |
| LOBS | : Dodecanoyloxybenzene sulfonate in the form of the Na salt. |
| DOBA | : Dodecanoylbenzoic acid |
| DTPA | : Diethylene triamine pentaacetic acid. |
| HEDP | : 1,1-hydroxyethane diphosphonic acid. |
| DETPMP | : Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060. |
| EDDS | : Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt |
| MnTACN | : Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane. |
| Photoactivated Bleach | : Sulfonated zinc or alumino phtalocyanine encapsulated in dextrin soluble polymer. |
| PAAC | : Pentaamine acetate cobalt(III) salt. |
| Paraffin | : Paraffin oil sold under the tradename Winog 70 by Wintershall. |
| NaBz | : Sodium benzoate. |

- Protease : Proteolytic enzyme sold under the tradename Savinase, Alcalase by Novo Nordisk A/S, the "protease D" variant with the substitution set N76D/S103A/V104I and the protease described in PCT application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 with the amino acid substitution set 101G/103A/104I/159D/232V/236H/245R/248D/252K.
- Amylase : Amylolytic enzyme sold under the tradename Termamyl® and Duramyl® available from Novo Nordisk A/S and those variants having improved thermal stability with amino acid deletions R181 + G182 or T183 + G184 as described in WO95/35382.
- Lipase : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
- Ra/Ga-AMG : Amyloglucosidase from *Rhizopus niveaus* sold by Amano under the tradename Gluczyme.
- Ra/Ga-Amylase : Alpha-amylase from *Lipomyces kononenkoae* from LKA1 gene.
- Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
- CMC : Sodium carboxymethyl cellulose.
- PVP : Polyvinyl polymer, with an average molecular weight of 60,000.
- PVNO : Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.
- PVPVI : Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl) stilbene-2,2'-disulfonate.
- Brightener 3 : Disodium 4,4'-bis (4,6-dianilino-1,3,5-triazin-2-yl)amino stilbene-2,2'-disulfonate.

- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
- Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
- Thickener : High molecular weight crosslinked polyacrylates such as Carbopol offered by B.F. Goodrich Chemical Company and Polygel.
- SRP 1 : Anionically end capped poly esters.
- SRP 2 : Soil Release Polymer selected from 1) Non-cotton soil release polymer according to U.S. Patent 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995 or and/or from 2) Non-cotton soil release polymer according to US application no.60/051517.
- QEA : $\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) \text{---} \text{N}^+\text{---}\text{C}_6\text{H}_{12}\text{---}\text{N}^+\text{---}(\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O})\text{---}(\text{C}_2\text{H}_4\text{O}))_n$, wherein $n =$ from 20 to 30.
- PEI : Polyethyleneimine with an average molecular weight of between 600-1800 and an average ethoxylation degree of 7-20 ethyleneoxy residues per nitrogen.
- SCS : Sodium cumene sulphonate.
- HMWPEO : High molecular weight polyethylene oxide.
- PEG X : Polyethylene glycol, of a molecular weight of X
- PEO : Polyethylene oxide, with an average molecular weight of 5,000.
- TEPAE : Tetraethylenepentaamine ethoxylate.
- BTA : Benzotriazole.
- PH : Measured as a 1% solution in distilled water at 20°C.

Example 1

The following granular laundry detergent compositions were prepared according to the present invention :

| | I | II | III | IV | V |
|-----------------------------|------|------|------|-----|-----|
| <u>Spray-dried Granules</u> | | | | | |
| LAS | 10.0 | 10.0 | 15.0 | 5.0 | 5.0 |
| TAS | - | 1.0 | - | - | - |

| | I | II | III | IV | V |
|---|------|------|------|------|------|
| MBAS | - | - | - | 5.0 | 5.0 |
| C45AS | - | - | 1.0 | - | 2.0 |
| C45AE ₃ S | - | - | - | 1.0 | - |
| QAS | - | - | 1.0 | 1.0 | - |
| DTPA, HEDP and/or EDDS | 0.3 | 0.3 | 0.5 | 0.3 | - |
| Mg Sulfate | 0.5 | 0.5 | 0.1 | - | - |
| Citrate | - | - | - | 3.0 | 5.0 |
| Carbonate | 10.0 | 7.0 | 15.0 | - | - |
| Sulphate | 5.0 | 5.0 | - | - | 5.0 |
| Silicate | - | - | - | - | 2.0 |
| Zeolite A | 16.0 | 18.0 | 20.0 | 20.0 | - |
| SKS-6 | - | - | - | 3.0 | 5.0 |
| MA/AA or AA | 1.0 | 2.0 | 11.0 | - | - |
| PEG 4000 | - | 2.0 | - | 1.0 | - |
| QEA | 1.0 | - | - | - | 1.0 |
| Brightener 1 or 2 or 3 | 0.05 | 0.05 | 0.05 | - | 0.05 |
| Silicone oil | 0.01 | 0.01 | 0.01 | - | - |
| <u>Agglomerate</u> | | | | | |
| Carbonate | - | - | - | - | 4.0 |
| SKS-6 | 6.0 | - | - | - | 6.0 |
| LAS | 4.0 | 5.0 | - | - | 5.0 |
| <u>Dry-add particulate components</u> | | | | | |
| Maleic acid / carbonate / bicarbonate (40:20:40) | 8.0 | 10.0 | 10.0 | 4.0 | - |
| QEA | - | - | - | 0.2 | 0.5 |
| NACA-OBS | 3.0 | - | - | 4.5 | - |
| NOBS | 1.0 | 3.0 | 3.0 | - | - |
| TAED | 2.5 | - | - | 1.5 | 2.5 |
| MBAS | - | - | - | 8.0 | - |
| LAS (flake) | 10.0 | 10.0 | - | - | - |
| <u>Spray-on</u> | | | | | |
| Brightener 1 or 2 or 3 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 |
| Perfume | 1.0 | 0.5 | 1.1 | 0.8 | 0.3 |
| <u>Dry-add</u> | | | | | |
| Citrate | - | - | 20.0 | 4.0 | - |

| | I | II | III | IV | V |
|--|------|------|-------|-------|------|
| Percarbonate | 15.0 | 3.0 | 6.0 | 10.0 | - |
| Perborate | - | - | - | - | 6.0 |
| Photoactivated bleach | 0.02 | 0.02 | 0.02 | 0.1 | 0.05 |
| Enzymes (cellulase, amylase, protease and/or lipase) | 0.04 | 0.01 | 0.02 | 0.02 | 0.05 |
| Ra/Ga-AMG | 1.0 | 0.05 | 0.002 | 0.001 | 0.05 |
| Carbonate | 0.0 | 10.0 | - | - | - |
| Perfume (encapsulated) | - | 0.5 | 0.5 | - | 0.3 |
| Suds suppressor | 1.0 | 0.6 | 0.3 | - | 0.10 |
| Soap | 0.5 | 0.2 | 0.3 | 3.0 | 0.5 |
| Citric | - | - | - | 6.0 | 6.0 |
| SKS-6 | - | - | - | 4.0 | - |

Fillers up to 100%

Example 2

The following granular laundry detergent compositions were prepared according to the present invention :

| | I | II | III | IV |
|------------------------|------|------|------|------|
| <u>Blown powder</u> | | | | |
| MES | 2.0 | 0.5 | 1.0 | - |
| SADS | - | - | - | 2.0 |
| LAS | 6.0 | 5.0 | 11.0 | 6.0 |
| TAS | 2.0 | - | - | 2.0 |
| Zeolite A | 24.0 | - | - | 20.0 |
| STPP | - | 27.0 | 24.0 | - |
| Sulfate | 4.0 | 6.0 | 13.0 | - |
| MA/AA | 1.0 | 4.0 | 6.0 | 2.0 |
| Silicate | 1.0 | 7.0 | 3.0 | 3.0 |
| CMC | 1.0 | 1.0 | 0.5 | 0.6 |
| Brightener 1 | 0.2 | 0.2 | 0.2 | 0.2 |
| Silicone antifoam | 1.0 | 1.0 | 1.0 | 0.3 |
| DTPMP | 0.4 | 0.4 | 0.2 | 0.4 |
| <u>Spray on</u> | | | | |
| Brightener 1 or 2 or 3 | 0.02 | - | - | 0.02 |
| C45E7 | - | - | - | 5.0 |

| | I | II | III | IV |
|-------------------------|-------|------------|-------|-------|
| C45E2 | 2.5 | 2.5 | 2.0 | - |
| C45E3 | 2.6 | 2.5 | 2.0 | - |
| Perfume | 0.5 | 0.3 | 0.5 | 0.2 |
| Silicone antifoam | 0.3 | 0.3 | 0.3 | - |
| <u>Dry additives</u> | | | | |
| QEA | - | - | - | 1.0 |
| EDDS | 0.3 | - | - | - |
| Sulfate | 2.0 | 3.0 | 5.0 | 10.0 |
| Carbonate | 6.0 | 13.0 | 15.0 | 14.0 |
| Citric | 2.5 | - | - | 2.0 |
| QAS | 0.5 | - | - | 0.5 |
| SKS-6 | 10.0 | - | - | - |
| Percarbonate | 4.0 | 3.0 | - | 1.9 |
| PB4 | - | - | - | - |
| NOBS | 0.5 | - | - | 0.3 |
| TAED | 0.75 | 4.5 | - | 0.5 |
| Clay | - | - | 10.0 | - |
| Protease | 0.03 | 0.03 | 0.03 | 0.03 |
| Lipase | 0.008 | 0.008 | 0.008 | 0.004 |
| Ra/Ga-AMG | 0.001 | 0.01 | - | 0.004 |
| Ra/Ga Amylase | - | 0.005 | 0.01 | - |
| Amylase | 0.003 | - | 0.003 | - |
| Brightener 1 | 0.05 | - | - | 0.05 |
| Misc/minor and speckles | | up to 100% | | |

Example 3

The following granular laundry detergent compositions were prepared according

5 to the invention :

| | I | II | III | IV | V | VI |
|---------------------|------|-----|-----|-----|-----|-----|
| <u>Blown powder</u> | | | | | | |
| LAS | 23.0 | 8.0 | 7.0 | 9.0 | 7.0 | 7.0 |
| QAS | - | - | - | - | 1.0 | - |
| C45AS | 6.0 | 6.0 | 5.0 | 8.0 | - | - |
| C45AE11S | - | 1.0 | 1.0 | 1.0 | - | - |
| MES | 2.0 | - | - | - | 2.0 | 4.0 |

| | I | II | III | IV | V | VI |
|----------------------|------|------|------|------|------|------|
| Zeolite A | 10.0 | 18.0 | 14.0 | 12.0 | 10.0 | 10.0 |
| MA/AA | - | 0.5 | - | - | - | 2.0 |
| MA/AA 1 | 7.0 | - | - | - | - | - |
| AA | - | 3.0 | 3.0 | 2.0 | 3.0 | 3.0 |
| Sulfate | 5.0 | 6.3 | 11.1 | 11.0 | 11.0 | 18.1 |
| Silicate | 10.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Carbonate | 15.0 | 20.0 | 10.0 | 20.7 | 8.0 | 6.0 |
| PEG 4000 | 0.4 | 1.5 | 1.5 | 1.0 | 1.0 | 1.0 |
| DTPA | - | 0.9 | 0.5 | - | - | 0.5 |
| Brightener 2 | 0.3 | 0.2 | 0.3 | - | 0.1 | 0.3 |
| <u>Spray on</u> | | | | | | |
| C45E7 | - | 2.0 | - | - | 2.0 | 2.0 |
| C25E9 | 3.0 | - | - | - | - | - |
| C23E9 | - | - | 1.5 | 2.0 | - | 2.0 |
| Perfume | 0.3 | 0.3 | 0.3 | 2.0 | 0.3 | 0.3 |
| <u>Agglomerates</u> | | | | | | |
| C45AS | - | 5.0 | 5.0 | 2.0 | - | 5.0 |
| LAS | - | 2.0 | 2.0 | - | - | 2.0 |
| Zeolite A | - | 7.5 | 7.5 | 8.0 | - | 7.5 |
| Carbonate | - | 4.0 | 4.0 | 5.0 | - | 4.0 |
| PEG 4000 | - | 0.5 | 0.5 | - | - | 0.5 |
| Misc (water etc) | - | 2.0 | 2.0 | 2.0 | - | 2.0 |
| <u>Dry additives</u> | | | | | | |
| QAS I | - | - | - | - | 1.0 | - |
| Citric | - | - | - | - | 2.0 | - |
| PB4 | - | - | - | - | 5 | - |
| PB1 | - | - | 4 | 1.0 | - | - |
| Percarbonate | 2.0 | - | - | 1.0 | - | 2.0 |
| Carbonate | - | 5.3 | 1.8 | - | 4.0 | 4.0 |
| NOBS | 0.5 | - | 0.4 | 0.3 | - | - |
| Clay | - | - | - | - | - | 10.0 |
| TAED | 0.6 | 0.4 | 0.6 | 0.3 | 0.9 | - |
| Methyl cellulose | 0.2 | - | - | - | - | 0.5 |
| DTPA | 0.7 | 0.5 | 1.0 | 0.5 | 0.5 | 1.2 |
| speckle | - | - | - | 0.2. | 0.5 | - |

| | I | II | III | IV | V | VI |
|----------------------|--------|--------|--------|--------|--------|--------|
| SKS-6 | 8.0 | - | - | - | - | - |
| STS | - | - | 2.0 | - | 1.0 | - |
| Cumene sulfonic acid | - | 1.0 | - | - | - | 2.0 |
| Lipase | 0.004 | - | 0.004 | - | 0.004 | 0.008 |
| Cellulase | 0.0005 | 0.0005 | 0.0005 | 0.0007 | 0.0005 | 0.0005 |
| Amylase | 0.003 | - | 0.001 | - | - | - |
| Ra/Ga-Amylase | - | 0.01 | - | - | 0.001 | 0.01 |
| Ra/Ga-AMG | 0.01 | - | 0.05 | 0.002 | 0.001 | 0.05 |
| Protease | 0.01 | 0.015 | 0.015 | 0.009 | 0.01 | 0.01 |
| PVPVI | - | - | - | - | 0.5 | 0.1 |
| PVP | - | - | - | - | 0.5 | - |
| PVNO | - | - | 0.5 | 0.3 | - | - |
| QEA | - | - | - | - | 1.0 | - |
| SRP1 | 0.2 | 0.5 | 0.3 | - | 0.2 | - |
| Silicone antifoam | 0.2 | 0.4 | 0.2 | 0.4 | 0.1 | - |
| Mg sulfate | - | - | 0.2 | - | 0.2 | - |

Misc/minors up to 100%

Example 4

The following granular laundry detergent compositions were prepared according to the present invention:

| | I | II | III | IV |
|---------------------|------|------|------|------|
| <u>Base granule</u> | | | | |
| STPP | - | 22.0 | - | 15.0 |
| Zeolite A | 30.0 | - | 24.0 | 5.0 |
| Sulfate | 5.5 | 5.0 | 7.0 | 7.0 |
| MA/AA | 3.0 | - | - | - |
| AA | - | 1.6 | 2.0 | - |
| MA/AA 1 | - | 12.0 | - | 6.0 |
| LAS | 14.0 | 10.0 | 9.0 | 20.0 |
| C45AS | 8.0 | 7.0 | 9.0 | 7.0 |
| C45AE11S | - | 1.0 | - | 1.0 |
| MES | 0.5 | 4.0 | 6.0 | - |
| SADS | 2.5 | - | - | 1.0 |

| | I | II | III | IV |
|----------------------|--------|--------|--------|--------|
| Silicate | - | 1.0 | 0.5 | 10.0 |
| Soap | - | 2.0 | - | - |
| Brightener 1 | 0.2 | 0.2 | 0.2 | 0.2 |
| Carbonate | 6.0 | 9.0 | 8.0 | 10.0 |
| PEG 4000 | - | 1.0 | 1.5 | - |
| DTPA | - | 0.4 | - | - |
| <u>Spray on</u> | | | | |
| C25E9 | - | - | - | 5.0 |
| C45E7 | 1.0 | 1.0 | - | - |
| C23E9 | - | 1.0 | 2.5 | - |
| Perfume | 0.2 | 0.3 | 0.3 | - |
| <u>Dry additives</u> | | | | |
| Carbonate | 5.0 | 10.0 | 13.0 | 8.0 |
| PVPVI/PVNO | 0.5 | - | 0.3 | - |
| Protease | 0.03 | 0.03 | 0.03 | 0.015 |
| Lipase | 0.008 | - | - | 0.008 |
| Ra/Ga-AMG | 0.01 | - | 0.05 | 0.005 |
| Ra/Ga-Amylase | - | 0.01 | 0.02 | 0.001 |
| Amylase | 0.002 | - | - | 0.002 |
| Cellulase | 0.0002 | 0.0005 | 0.0005 | 0.0003 |
| DTPA | 0.5 | 0.3 | 0.5 | 1.0 |
| LOBS | - | 0.8 | - | 0.3 |
| PB1 | 5 | 3.0 | 10 | 4.0 |
| DOBA | 1.0 | - | 0.4 | - |
| TAED | 0.5 | 0.3 | 0.5 | 0.6 |
| Sulfate | 4.0 | 5.0 | - | 5.0 |
| SRP 1 | - | 0.4 | - | - |
| Suds supressor | - | 0.5 | - | - |
| speckle | 09 | - | 2.7 | 1.2 |
| Misc/minor to 100% | | | | |

Example 5

The following granular laundry detergent compositions were prepared according to the present invention :

I II III IV IV V VI

| | I | II | III | IV | IV | V | VI |
|---|------------|------|------|------|------|------|------|
| C ₁₃ LAS | 12.0 | 16.0 | 23.0 | 19.0 | 18.0 | 20.0 | 16.0 |
| C ₄₅ AS | | 4.5 | - | | - | - | 4.0 |
| C ₄₅ AE (3)S | - | - | 2.0 | - | 1.0 | 1.0 | 1.0 |
| C ₄₅ AE (3.0) | 2.0 | 2.0 | - | 1.3 | - | - | 0.6 |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | | | - | - | 1.0 | 0.5 | 2.0 |
| Tallow fatty acid | - | - | - | - | - | - | 1.0 |
| STPP | 23.0 | 25.0 | 24.0 | 22.0 | 20.0 | 15.0 | 20.0 |
| Carbonate | 15.0 | 12.0 | 15.0 | 10.0 | 13.0 | 11.0 | 10.0 |
| AA | 0.5 | 0.5 | 0.5 | 0.5 | - | - | - |
| MA/AA | - | - | 1.0 | 1.0 | 1.0 | 2.0 | 0.5 |
| Silicate | 3.0 | 6.0 | 9.0 | 8.0 | 9.0 | 6.0 | 8.0 |
| Sulfate | 25.0 | 18.0 | 20.0 | 18.0 | 20.0 | 22.0 | 13.0 |
| Sodium perborate | 5.0 | 5.0 | 10.0 | 8.0 | 3.0 | 1.0 | 2.0 |
| PEG 4000 | 1.5 | 1.5 | 1.0 | 1.0 | - | - | 0.5 |
| CMC | 1.0 | 1.0 | 1.0 | - | 0.5 | 0.5 | 0.5 |
| Citric | - | - | - | - | - | - | - |
| NOBS/ DOBS | 0.5 | 1.0 | 0.5 | 0.5 | 1.0 | 0.7 | 0.3 |
| TAED | 1.5 | 1.0 | 2.5 | 3.0 | 0.3 | 0.2 | 0.5 |
| SRP 2 | 1.5 | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Moisture | 7.5 | 7.5 | 6.0 | 7.0 | 5.0 | 3.0 | 5.0 |
| Mg | - | - | - | - | 1.0 | 0.5 | 1.5 |
| DTPA, HEDP and/or EDDS | - | - | - | - | 0.8 | 0.6 | 1.0 |
| Ra/Ga-AMG | 0.01 | 0.01 | .005 | 0.05 | 1.0 | 1.0 | .001 |
| Enzymes (amylase, cellulase and/or protease) | - | - | - | - | 0.05 | 0.04 | 0.05 |
| Minors, e.g. perfume, Brightener, photo-bleach, speckles | Up to 100% | | | | | | |

Example 6

The following granular laundry detergent compositions were prepared according to the present invention:

I II III IV

| | I | II | III | IV |
|--|------|------------|-------|-------|
| C ₁₃ LAS | 13.3 | 13.7 | 10.4 | 8.0 |
| C ₄₅ AS | 3.9 | 4.0 | 4.5 | - |
| C ₄₅ AE (0.5)S | 2.0 | 2.0 | - | - |
| C ₄₅ AE (6.5) | 0.5 | 0.5 | 0.5 | 5.0 |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | 1.0 | - | - | 0.5 |
| Tallow fatty acid | 0.5 | - | - | - |
| Tallow alcohol ethoxylate (50) | - | - | 1.0 | 0.3 |
| STPP | - | 41.0 | - | 20.0 |
| Zeolite A | 26.3 | - | 21.3 | 1.0 |
| Carbonate | 23.9 | 12.4 | 25.2 | 17.0 |
| AA | 3.4 | 0.0 | 2.7 | - |
| MA/AA | - | - | 1.0 | 1.5 |
| Silicate | 2.4 | 6.4 | 2.1 | 6.0 |
| Sulfate | 10.5 | 10.9 | 8.2 | 15.0 |
| Sodium perborate | 1.0 | 1.0 | 1.0 | 2.0 |
| PEG 4000 | 1.7 | 0.4 | 1.0 | - |
| CMC | 1.0 | - | - | 0.3 |
| Citric | - | - | 3.0 | - |
| NOBS/ DOBS | 0.2 | 0.5 | 0.5 | 0.1 |
| TAED | 0.6 | 0.5 | 0.4 | 0.3 |
| SRP 2 | 1.5 | 1.5 | 1.0 | 1.0 |
| Moisture | 7.5 | 3.1 | 6.1 | 7.3 |
| Mg sulphate | - | - | - | 1.0 |
| DTPA, HEDP and/or EDDS | - | - | - | 0.5 |
| Enzymes (amylase, cellulase, protease and/or lipase) | - | 0.025 | - | 0.04 |
| Ra/Ga-Amylase | - | 0.005 | - | 0.008 |
| Ra/Ga-AMG | 0.02 | - | 0.005 | 0.008 |
| Misc / Minors including perfume, brightener, photo-bleach | | Up to 100% | | |

Example 7

The following laundry detergent compositions in the form of a tablet or granular formulation were prepared according to the present invention :

| | I | II | III | IV | V | VI |
|---|------|------|------|------|------|------|
| C ₁₃ LAS | 20.0 | 16.0 | 8.5 | 5 | 20.0 | 6.0 |
| C ₄₅ AS | - | 4.0 | - | - | - | - |
| C ₄₅ AE(3)S | 1.0 | 1.0 | - | - | - | - |
| C ₄₅ AE | - | 5.0 | 5.5 | 4.0 | - | - |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | 0.5 | 2.0 | - | - | - | - |
| Tallow fatty acid | - | 1.0 | - | - | - | - |
| STPP / Zeolite | 10.0 | 20.0 | 30.0 | 20.0 | 25.0 | 25.0 |
| Carbonate | 41.0 | 30.0 | 30.0 | 25.0 | 45.0 | 24.0 |
| AA | - | - | - | - | - | - |
| MA/AA | 2.0 | 0.5 | 0.5 | 1.0 | - | - |
| Silicate | 6.0 | 8.0 | 5.0 | 6.0 | 8.0 | 5.0 |
| Sulfate | 2.0 | 3.0 | - | - | - | 8.0 |
| Sodium perborate/ percarbonate | 1.0 | - | 20.0 | 14.0 | - | - |
| PEG 4000 | - | 0.5 | - | - | - | 0.5 |
| CMC | 0.5 | 0.5 | 0.5 | 0.5 | - | 0.5 |
| Citric | - | - | - | - | - | - |
| NOBS/ DOBS | 0.7 | - | - | - | - | - |
| TAED / Preformed peracid | 0.7 | - | 4.5 | 5.0 | - | - |
| DTPA, HEDP and/or EDDS | - | - | 0.5 | 0.5 | - | - |
| SRP | 1.0 | - | 1.0 | 1.0 | - | - |
| Clay | 4.0 | 3.0 | 7.0 | 10.0 | 6.0 | 8.0 |
| PEO | 1.0 | 0.5 | 2.0 | 0.5 | 1.0 | 0.5 |
| Humectant | 0.5 | - | - | 0.5 | - | - |
| wax | 0.5 | - | - | 0.5 | - | - |
| Cellulose | 2.0 | - | - | 1.5 | - | 1.0 |
| Sodium acetate | - | - | 1.0 | 0.5 | 4.0 | 1.0 |
| Moisture | 3.0 | 5.0 | 5.0 | 5.0 | 8.0 | 10.0 |
| Mg sulphate | 0.5 | 1.5 | - | - | - | - |
| Soap/ suds suppressor | 0.6 | 1.0 | 1.0 | 0.8 | 0.5 | - |
| Enzymes (amylase, cellulase, protease and/or lipase) | 0.04 | 0.04 | 0.01 | 0.02 | 0.02 | 0.03 |
| Ra/Ga-AMG | 0.03 | 0.01 | 0.05 | - | - | - |

| | I | II | III | IV | V | VI |
|---|---|----|------------|------|-----|------|
| Ra/Ga-Amylase | - | - | 0.02 | .003 | 0.1 | .002 |
| Minors, e.g. perfume, PVP, PVPVI/PVNO, brightener, photo-bleach, speckles,... | | | Up to 100% | | | |

5

Example 8

The following laundry detergent compositions were prepared according to the present invention :

| | I | II | III | IV | V |
|---|------|------|------|------|------|
| C ₁₃ LAS | 12.0 | 16.0 | 23.0 | 19.0 | 18.0 |
| C ₄₅ AS | - | 4.5 | - | - | - |
| C ₄₅ AE(3)S | - | - | 2.0 | - | 1.0 |
| C ₄₅ AE | 2.0 | 2.0 | - | 1.3 | - |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | - | - | - | - | 1.0 |
| STPP / Zeolite | 23.0 | 25.0 | 14.0 | 22.0 | 20.0 |
| Carbonate | 25.0 | 22.0 | 35.0 | 20.0 | 28.0 |
| AA | 0.5 | 0.5 | 0.5 | 0.5 | - |
| MA/AA | - | - | 1.0 | 1.0 | 1.0 |
| Silicate | 3.0 | 6.0 | 9.0 | 8.0 | 9.0 |
| Sodium perborate/ percarbonate | 5.0 | 5.0 | 10.0 | - | 3.0 |
| PEG 4000 | 1.5 | 1.5 | 1.0 | 1.0 | - |
| CMC | 1.0 | 1.0 | 1.0 | - | 0.5 |
| NOBS/ DOBS | - | 1.0 | - | - | 1.0 |
| TAED / Preformed peracid | 1.5 | 1.0 | 2.5 | - | 3.0 |
| DTPA, HEDP and/or EDDS | 0.5 | 0.5 | 0.5 | - | 1.0 |
| SRP | 1.5 | 1.5 | 1.0 | 1.0 | - |
| Clay | 5.0 | 6.0 | 12.0 | 7.0 | 10.0 |
| Flocculating agent PEO | 0.2 | 0.2 | 3.0 | 2.0 | 0.1 |

| | I | II | III | IV | V |
|--|------------|------|------|------|-------|
| Humectant | - | - | - | - | 0.5 |
| wax | 0.5 | - | - | - | - |
| Cellulose | 0.5 | 2.0 | - | - | 3.0 |
| Sodium acetate | 2.0 | 1.0 | 3.0 | - | - |
| Moisture | 7.5 | 7.5 | 6.0 | 7.0 | 5.0 |
| Soap/ suds suppressor | - | - | 0.5 | 0.5 | 0.8 |
| Ra/Ga-Amylase | 0.005 | 0.02 | - | - | 0.01 |
| Ra/Ga-AMG | - | - | .005 | .005 | 0.01 |
| Enzymes (amylase, cellulase, protease and/or lipase) | - | - | - | - | 0.045 |
| Misc / Minors, e.g. perfume, PVP, PVPVI/PVNO, speckles, brightener, photo-bleach,... | Up to 100% | | | | |

Example 9

The following liquid laundry detergent compositions were prepared according to the present invention :

| | I | II | III | IV | V | VI |
|---------------------|------|------|------|------|------|-----|
| LAS | - | - | - | 1.0 | 2.0 | - |
| C25AS | 16.0 | 13.0 | 14.0 | 5.0 | - | 6.5 |
| C25AE3S | 5.0 | 1.0 | - | 10.0 | 19.0 | 3.0 |
| C25E7 | 2.0 | 3.5 | - | 2.5 | 2.0 | 5.0 |
| TFAA | 5.0 | 4.5 | 4.5 | 6.5 | 4.0 | - |
| APA | 2.0 | 1.0 | - | 3.0 | - | 0.5 |
| QAS | - | - | 2.0 | - | 1.5 | - |
| TPKFA | 4.5 | 8.0 | 15.0 | - | 5.0 | 5.0 |
| Citric | 2.2 | 3.0 | - | 0.5 | 1.0 | 2.0 |
| Rapeseed fatty acid | 2.0 | - | - | 3.0 | 6.0 | 1.5 |
| Ethanol | 3.2 | 2.0 | 2.5 | 2.2 | - | 0.5 |
| 1,2 Propandiol | 5.7 | 8.5 | 6.5 | 7.0 | 7.0 | 5.5 |
| Monoethanolamine | 5.0 | 7.5 | - | 5.0 | 1.0 | 2.0 |
| TEPAE | - | 1.2 | - | 0.5 | 0.5 | - |
| PEI2 | - | 1.5 | - | 1.0 | 0.8 | - |
| DTPMP | 1.3 | 0.5 | 0.8 | 0.5 | - | 0.2 |
| HEDP | - | 0.5 | 0.2 | 1.0 | - | - |

| | I | II | III | IV | V | VI |
|------------------|-------|-------|-------|-------|-------|-------|
| Protease | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 | 0.01 |
| Ra/Ga-Amylase | 0.01 | - | 0.01 | 0.005 | - | - |
| Ra/Ga-AMG | - | 0.02 | - | 0.01 | 0.005 | 0.002 |
| Lipase | 0.002 | 0.001 | 0.001 | - | 0.001 | - |
| Amylase | - | .0006 | - | - | 0.001 | - |
| Cellulase | 0.002 | 0.002 | - | 0.002 | 0.001 | - |
| SRP1 | 0.20 | 0.15 | 0.10 | - | 0.17 | 0.04 |
| PVNO | - | - | - | 0.05 | 0.10 | - |
| Brightener 3 | 0.20 | 0.15 | 0.10 | 0.05 | - | 0.05 |
| Suds Suppressor | 0.25 | 0.20 | 0.15 | 0.15 | 0.30 | 0.10 |
| Calcium Chloride | 0.02 | 0.02 | - | 0.01 | 0.01 | - |
| Boric acid | 2.5 | 2.0 | 1.5 | 2.2 | 1.5 | 1.2 |
| Bentonite Clay | - | - | 5.5 | - | - | - |
| NaOH to pH | 8.0 | 7.5 | 7.7 | 8.0 | 7.0 | 7.5 |

Water/minors to 100%

Example 10

- 5 The following non-aqueous liquid detergent compositions were prepared in accordance with the present invention :

| | I | II | III |
|---|------|------|------|
| LAS | 16.0 | 16.0 | 16.0 |
| C23 E05S | 21.5 | 21.5 | 19.0 |
| Butoxy Propoxy Propanol | 18.5 | - | 16.0 |
| Hexylene Glycol | - | 18.5 | 5.0 |
| Sodium citrate dihydrate | 6.8 | 6.8 | 3.8 |
| [NACA-OBS] Na salt | 6.0 | 6.0 | 6.0 |
| Methyl sulfate salt of methyl quaternized polyethoxylated hexamethylene diamine | 1.3 | 1.3 | 1.3 |
| EDDS | 1.2 | 1.2 | 1.2 |
| MA/AA | - | - | 3.0 |
| Sodium Carbonate | 10.0 | 10.0 | 10.0 |
| Protease | 0.05 | 0.02 | 0.02 |
| Ra/Ga-Amylase | 0.01 | - | 0.05 |
| Ra/Ga-AMG | - | 0.01 | 0.02 |

| | I | II | III |
|---|--------|--------|--------|
| Amylase | 0.01 | 0.01 | 0.01 |
| Cellulase | 0.0001 | 0.0001 | 0.0001 |
| PB1 | 12.0 | 12.0 | 12.0 |
| Silicone antifoam | 0.75 | 0.75 | 1.1 |
| Perfume | 1.7 | 1.7 | 1.7 |
| Titanium Dioxide | 0.5 | 0.5 | 0.5 |
| Dichloro -5,12-Dimethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane | - | 0.03 | 0.03 |
| Manganese (II) | | | |
| Brightener 2 | 0.2 | 0.2 | 0.2 |
| Sodium hydrogenated C16-18 fatty soap | 1 | 1 | 0.5 |
| Colored Speckles | 0.4 | 0.4 | 0.4 |
| Miscellaneous up to 100% | | | |

Example 11

The following laundry detergent compositions in the form of a tablet were prepared according to the present invention :

- i) a detergent base powder of composition I was prepared as follows: all the particulate material of base composition I were mixed together in a mixing drum to form a homogenous particulate mixture. During this mixing, the spray-ons were carried out.
- ii) Tablets were then made the following way: 50g of the matrix was introduced into a mould of circular shape with a diameter of 5.5 cm, and compressed to give a tablet tensile strength (or diametrical fracture stress) of 10kPa.
- iii) The tablets were then dipped in a bath comprising 90 parts of sebacic acid and 10 parts per weight of Nymcel-ZSB16™ by Metsa Serla at 140 °C. The time the tablet was dipped in the heated bath was adjusted to allow application of 4g of the bath mixture. The tablet was then left to cool at ambient temperature of 25°C for 24 hours. The tensile strength of the coated tablet was increased to a tensile strength of 30 kPa.

Anionic agglomerates 1 (40% anionic, 27% zeolite and 33% carbonate) 21.5

| | |
|---|--------|
| | I |
| Anionic agglomerates 2 (40% anionic, 28% zeolite and 32% carbonate) | 13.0 |
| Cationic agglomerates (20% cationic, 56% zeolite and 24% sulphate) | 5.5 |
| Layered silicate (95% SKS 6 and 5% silicate) | 10.8 |
| Sodium percarbonate | 14.2 |
| Bleach activator agglomerates (81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water) | 5.5 |
| Carbonate | 10.98 |
| EDDS/Sulphate particle (58% of EDDS, 23% of sulphate and 19% water) | 0.5 |
| HEDP | 0.8 |
| SRP | 0.3 |
| Fluorescer | 0.2 |
| Photoactivated bleach (Zinc phthalocyanine sulphonate 10% active) | 0.02 |
| Soap powder | 1.4 |
| Suds suppressor (11.5% silicone oil; 59% of zeolite and 29.5% of water) | 1.9 |
| Citric | 7.1 |
| Ra/Ga-Amylase | 0.05 |
| Protease | 0.03 |
| Lipase | 0.006 |
| Cellulase | 0.0005 |
| Amylase | 0.02 |
| Binder spray-on system (25% of Lutensit K-HD 96;75% by weight of PEG) | 4.0 |

Example 12

The following laundry detergent compositions in the form of a tablet were prepared according to the present invention :

| | | | | | | |
|--------------------|------|------|------|------|------|------|
| | I | II | III | IV | V | VI |
| <u>First Phase</u> | | | | | | |
| Percarbonate | 45.0 | 45.0 | 45.0 | 45.0 | 45.0 | 45.0 |
| TAED | 9.7 | 9.7 | 9.7 | 9.7 | 9.7 | 9.7 |

| | | | | | | |
|---------------------|------|------|------|------|------|------|
| Citric acid | 10.0 | 15.0 | 20.0 | 15.0 | 15.0 | 15.0 |
| STPP | - | - | - | - | - | 6.0 |
| MA/AA | 6.0 | 6.0 | 1.0 | 5.0 | - | - |
| Silicates | - | - | - | - | 6.0 | - |
| Bicarbonate | 15.0 | 15.0 | 10.0 | 15.0 | 15.0 | 15.0 |
| Carbonate | 5.0 | - | - | - | - | - |
| Brightener 1 or 2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Perfume | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| C12-16 Fatty acid | - | - | - | 1.0 | - | - |
| Protease | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Amylase | 0.02 | 0.02 | - | 0.02 | - | - |
| <u>Second phase</u> | | | | | | |
| Ra/Ga-AMG | 0.01 | 0.02 | 0.04 | 0.01 | 0.1 | 0.5 |
| Protease | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |
| Amylase | 0.02 | 0.02 | - | - | - | - |
| Speckles | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| PEG 4000 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| Citric | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 |
| Bicarbonate | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 |

5 Example 13

The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

| | I | II | III | VI | V | III | VI | V |
|--------------|------|------|------|------|------|-------|------|------|
| LAS | - | - | 19.0 | 15.0 | 21.0 | 6.75 | 8.8 | - |
| C28AS | 30.0 | 13.5 | - | - | - | 15.75 | 11.2 | 22.5 |
| Na Laurate | 2.5 | 9.0 | - | - | - | - | - | - |
| Zeolite A | 2.0 | 1.25 | - | - | - | 1.25 | 1.25 | 1.25 |
| Carbonate | 20.0 | 3.0 | 13.0 | 8.0 | 10.0 | 15.0 | 15.0 | 10.0 |
| Ca Carbonate | 27.5 | 39.0 | 35.0 | - | - | 40.0 | - | 40.0 |
| Sulfate | 5.0 | 5.0 | 3.0 | 5.0 | 3.0 | - | - | 5.0 |
| TSPP | 5.0 | - | - | - | - | 5.0 | 2.5 | - |

| | I | II | III | VI | V | III | VI | V |
|--------------------------------|------|-------|------|-------|-------|-------|-------|-------|
| STPP | 5.0 | 15.0 | 10.0 | - | - | 7.0 | 8.0 | 10.0 |
| Bentonite clay | - | 10.0 | - | - | 5.0 | - | - | - |
| DETPMP | - | 0.7 | 0.6 | - | 0.6 | 0.7 | 0.7 | 0.7 |
| CMC | - | 1.0 | 1.0 | 1.0 | 1.0 | - | - | 1.0 |
| Talc | - | - | 10.0 | 15.0 | 10.0 | - | - | - |
| Silicate | - | - | 4.0 | 5.0 | 3.0 | - | - | - |
| PVNO | 0.02 | 0.03 | - | 0.01 | - | 0.02 | - | - |
| MA/AA | 0.4 | 1.0 | - | - | 0.2 | 0.4 | 0.5 | 0.4 |
| SRP 1 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Amylase | - | - | 0.01 | - | - | - | 0.002 | - |
| Ra/Ga-AMG | 0.01 | 0.1 | 0.02 | 0.002 | - | 0.01 | 0.01 | 0.002 |
| Ra/Ga-Amylase | - | - | - | - | 0.05 | - | 0.02 | 0.001 |
| Protease | - | 0.004 | - | 0.003 | 0.003 | - | - | 0.003 |
| Lipase | - | 0.002 | - | 0.002 | - | - | - | - |
| Cellulase | - | .0003 | - | - | .0003 | .0002 | - | - |
| PEO | - | 0.2 | - | 0.2 | 0.3 | - | - | 0.3 |
| Perfume | 1.0 | 0.5 | 0.3 | 0.2 | 0.4 | - | - | 0.4 |
| Mg sulfate | - | - | 3.0 | 3.0 | 3.0 | - | - | - |
| Brightener | 0.15 | 0.1 | 0.15 | - | - | - | - | 0.1 |
| Photoactivated bleach (ppm) | - | 15.0 | 15.0 | 15.0 | 15.0 | - | - | 15.0 |

5 Example 14

The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

| | I | II |
|-------|-----|------|
| C45AS | - | 10.0 |
| LAS | 7.6 | - |
| C68AS | 1.3 | - |
| C45E7 | 4.0 | - |
| C25E3 | - | 5.0 |

| | I | II |
|---|------------|-------|
| Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride | 1.4 | 1.0 |
| Citrate | 5.0 | 3.0 |
| Na-SKS-6 | - | 11.0 |
| Zeolite A | 15.0 | 15.0 |
| MA/AA | 4.0 | 4.0 |
| DETPMP | 0.4 | 0.4 |
| PB1 | 15.0 | - |
| Percarbonate | - | 15.0 |
| TAED | 5.0 | 5.0 |
| Smectite clay | 10.0 | 10.0 |
| HMWPEO | - | 0.1 |
| Protease | 0.02 | 0.01 |
| Lipase | 0.02 | 0.01 |
| Ra/Ga-AMG | - | 0.02 |
| Ra/Ga-Amylase | 0.05 | - |
| Amylase | 0.03 | 0.005 |
| Cellulase | 0.001 | - |
| Silicate | 3.0 | 5.0 |
| Carbonate | 10.0 | 10.0 |
| Suds suppressor | 1.0 | 4.0 |
| CMC | 0.2 | 0.1 |
| Miscellaneous and minors | Up to 100% | |

Example 15

The following rinse added fabric softener composition was prepared according to

5 the present invention :

| | |
|-------------------|-------|
| DEQA (2) | 20.0 |
| Cellulase | 0.001 |
| Ra/Ga-AMG | 0.005 |
| HCL | 0.03 |
| Antifoam agent | 0.01 |
| Blue dye | 25ppm |
| CaCl ₂ | 0.20 |
| Perfume | 0.90 |

Miscellaneous and water

Up to 100%

Example 16

The following fabric softener and dryer added fabric conditioner compositions
5 were prepared according to the present invention :

| | I | II | III | IV | V |
|-----------------------|-------|-------|------|------|------|
| DEQA | 2.6 | 19.0 | - | - | - |
| DEQA(2) | - | - | - | - | 52.0 |
| DTMAMS | - | - | - | 26.0 | - |
| SDASA | - | - | 70.0 | 42.0 | 40.2 |
| Stearic acid of IV=0 | 0.3 | - | - | - | - |
| C45EO1-3 | - | - | 13.0 | - | - |
| HCL | 0.02 | 0.02 | - | - | - |
| Ethanol | - | - | 1.0 | - | - |
| Perfume | 0.3 | 1.0 | 0.75 | 1.0 | 1.5 |
| Glycoperse S-20 | - | - | - | - | 15.4 |
| Glycerol monostearate | - | - | - | 26.0 | - |
| Digeranyl Succinate | - | - | 0.38 | - | - |
| Silicone antifoam | 0.01 | 0.01 | - | - | - |
| Electrolyte | - | 0.1 | - | - | - |
| Amylase | - | 0.2 | - | 0.2 | 0.2 |
| Ra/Ga-AMG | 1.0 | 0.2 | 0.1 | 0.01 | 0.01 |
| Clay | - | - | - | 3.0 | - |
| Dye | 10ppm | 25ppm | 0.01 | - | - |
| Water and minors | 100% | 100% | - | - | - |

Example 17

The following compact high density (0.96Kg/l) dishwashing detergent
compositions were prepared according to the present invention :

| | I | II | III | IV | V | VI |
|--------------|------|------|------|------|------|------|
| STPP | - | 51.0 | 51.0 | - | - | 44.3 |
| Citrate | 17.0 | - | - | 50.0 | 40.2 | - |
| Carbonate | 17.5 | 14.0 | 20.0 | - | 8.0 | 33.6 |
| Bicarbonate | - | - | - | 26.0 | - | - |
| Silicate | 15.0 | 15.0 | 8.0 | - | 25.0 | 3.6 |
| Metasilicate | 2.5 | 4.5 | 4.5 | - | - | - |

| | I | II | III | IV | V | VI |
|----------------------------------|------------|-------|------|-------|-------|------|
| PB1 | 10.0 | 8.0 | 8.0 | - | - | - |
| PB4 | - | - | - | 10.0 | - | - |
| Percarbonate | - | - | - | - | 11.8 | 4.8 |
| Nonionic | 2.0 | 1.5 | 1.5 | 3.0 | 1.9 | 5.9 |
| TAED | 2.0 | - | - | 4.0 | - | 1.4 |
| HEDP | 1.0 | - | - | - | - | - |
| DETPMP | 0.6 | - | - | - | - | - |
| MnTACN | - | - | - | - | 0.01 | - |
| PAAC | - | 0.01 | 0.01 | - | - | - |
| Paraffin | 0.5 | 0.4 | 0.4 | 0.6 | - | - |
| Protease | 0.07 | 0.05 | 0.05 | 0.03 | 0.06 | 0.01 |
| Amylase | 0.01 | - | 0.01 | - | 0.02 | - |
| Ra/Ga-AMG | 0.02 | 0.2 | - | - | 0.002 | 0.02 |
| Ra/Ga-Amylase | - | - | 0.02 | 0.02 | - | - |
| Lipase | - | 0.001 | - | 0.005 | - | - |
| BTA | 0.3 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 |
| Polycarboxylate | 6.0 | - | - | - | 4.0 | 0.9 |
| Perfume | 0.2 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 |
| pH | 11.0 | 11.0 | 11.3 | 9.6 | 10.8 | 10.9 |
| Miscellaneous, sulfate and water | Up to 100% | | | | | |

Example 18

The following granular dishwashing detergent compositions of bulk density

- 5 1.02Kg/L were prepared according to the present invention :

| | I | II | III | IV | V | VI |
|--------------|------|-------|------|------|------|------|
| STPP | 30.0 | 33.5 | 27.9 | 29.6 | 33.8 | 22.0 |
| Carbonate | 30.5 | 30.5 | 30.5 | 23.0 | 34.5 | 45.0 |
| Silicate | 7.0 | 7.5 | 12.6 | 13.3 | 3.2 | 6.2 |
| Metasilicate | - | 4.5 | - | - | - | - |
| Percarbonate | - | - | - | - | 4.0 | - |
| PB1 | 4.4 | 4.5 | 4.3 | - | - | - |
| NADCC | - | - | - | 2.0 | - | 0.9 |
| Nonionic | 1.0 | 0.7 | 1.0 | 1.9 | 0.7 | 0.5 |
| TAED | 1.0 | - | - | - | 0.9 | - |
| PAAC | - | 0.004 | - | - | - | - |

| | I | II | III | IV | V | VI |
|----------------------------------|------------|-------|-------|------|-------|-------|
| Paraffin | 0.25 | 0.25 | - | - | - | - |
| Protease | 0.036 | 0.021 | 0.03 | - | 0.006 | - |
| Amylase | 0.03 | - | 0.004 | - | 0.005 | - |
| Ra/Ga-AMG | 0.2 | 0.02 | - | - | 0.02 | 0.005 |
| Ra/Ga-Amylase | - | - | 0.01 | 0.02 | - | 0.01 |
| Lipase | 0.005 | - | 0.001 | - | - | - |
| BTA | 0.15 | 0.15 | - | - | 0.2 | - |
| Perfume | 0.2 | 0.2 | 0.05 | 0.1 | 0.2 | - |
| pH | 10.8 | 11.3 | 11.0 | 10.7 | 11.5 | 10.9 |
| Miscellaneous, sulfate and water | Up to 100% | | | | | |

Example 19

- 5 The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

| | I | II | III | IV | V | VI | VII | VIII |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| STPP | - | 48.8 | 54.7 | 38.2 | - | 52.4 | 56.1 | 36.0 |
| Citrate | 20.0 | - | - | - | 35.9 | - | - | - |
| Carbonate | 20.0 | 5.0 | 14.0 | 15.4 | 8.0 | 23.0 | 20.0 | 28.0 |
| Silicate | 15.0 | 14.8 | 15.0 | 12.6 | 23.4 | 2.9 | 4.3 | 4.2 |
| Protease | 0.042 | 0.072 | 0.042 | 0.031 | 0.052 | 0.023 | 0.023 | 0.029 |
| Amylase | 0.012 | 0.012 | 0.012 | 0.007 | 0.015 | - | - | 0.002 |
| Ra/Ga-AMG | 0.02 | 0.01 | 0.002 | 0.5 | 0.008 | 0.002 | - | 0.02 |
| Ra/Ga-Amylase | 0.001 | - | - | - | - | 0.03 | 0.01 | - |
| Lipase | 0.005 | - | - | - | - | - | - | - |
| PB1 | 14.3 | 7.8 | 11.7 | 12.2 | - | - | 6.7 | 8.5 |
| PB4 | - | - | - | - | 22.8 | - | 3.4 | - |
| Percarbonate | - | - | - | - | - | 10.4 | - | - |
| Nonionic | 1.5 | 2.0 | 2.0 | 2.2 | 1.0 | 4.2 | 4.0 | 6.5 |
| PAAC | - | - | 0.02 | 0.009 | - | - | - | - |
| MnTACN | - | - | - | - | 0.007 | - | - | - |
| TAED | 2.7 | 2.4 | - | - | - | 2.1 | 0.7 | 1.6 |
| HEDP | 1.0 | - | - | 0.9 | - | 0.4 | 0.2 | - |
| DETPMP | 0.7 | - | - | - | - | - | - | - |
| Paraffin | 0.4 | 0.5 | 0.5 | 0.5 | - | - | 0.5 | - |

| | I | II | III | IV | V | VI | VII | VIII |
|----------------------------------|------------|------|------|------|------|------|------|------|
| BTA | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | - |
| Polycarboxylate | 4.0 | - | - | - | 4.9 | 0.6 | 0.8 | - |
| PEG 4,000-30,000 | - | - | - | - | - | 2.0 | - | 2.0 |
| Glycerol | - | - | - | - | - | 0.4 | - | 0.5 |
| Perfume | - | - | - | 0.05 | 0.2 | 0.2 | 0.2 | 0.2 |
| Weight of tablet | 20g | 25g | 20g | 30g | 18g | 20g | 25g | 24g |
| pH | 10.7 | 10.6 | 10.7 | 10.7 | 10.9 | 11.2 | 11.0 | 10.8 |
| Miscellaneous, sulfate and water | Up to 100% | | | | | | | |

Example 20

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

| | I | II | III | IV |
|-----------|------------|------|-------|------|
| STPP | 17.5 | 17.2 | 23.2 | 23.1 |
| Carbonate | - | 2.4 | - | - |
| Silicate | 6.1 | 24.9 | 30.7 | 22.4 |
| NaOCl | 1.1 | 1.1 | 1.1 | 1.2 |
| Thickener | 1.0 | 1.1 | 1.1 | 1.0 |
| Nonionic | - | 0.1 | 0.06 | 0.1 |
| NaBz | 0.7 | - | - | - |
| Ra/Ga-AMG | 0.005 | 1.0 | 0.005 | 0.02 |
| NaOH | 1.9 | - | - | - |
| KOH | 3.6 | 3.0 | - | - |
| Perfume | 0.05 | - | - | - |
| pH | 11.7 | 10.9 | 10.8 | 11.0 |
| Water | up to 100% | | | |

Example 21

The following dishwashing compositions in the tablet form were prepared according to the present invention (Levels are indicated in g):

| | I | II | III | IV | V | VI |
|----------------|-----|-----|------|-----|-----|------|
| Phase 1 | | | | | | |
| STPP | 9.6 | 9.6 | 10.4 | 9.6 | 9.6 | 11.5 |
| Silicate | 0.5 | 0.7 | 1.6 | 1.0 | 1.0 | 2.4 |

| | I | II | III | IV | V | VI |
|-------------------|--------|-------|--------|--------|-------|--------|
| SKS-6 | 1.5 | 1.50 | | 2.30 | 2.25 | |
| Carbonate | 2.3 | 2.7 | 3.5 | 3.6 | 4.1 | 5.2 |
| HEDP | 0.2 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 |
| PB1 | 2.4 | 2.4 | 2.4 | 3.7 | 3.7 | 3.7 |
| PAAC | 0.002 | 0.002 | 0.002 | 0.003 | 0.004 | 0.004 |
| Ra/Ga-AMG | 0.01 | 0.02 | 0.05 | 0.002 | 0.001 | - |
| Ra/Ga-Amylase | - | - | - | 0.01 | - | 0.01 |
| Amylase | 0.002 | 0.001 | - | - | - | - |
| Protease | 0.002 | 0.002 | 0.002 | 0.003 | 0.003 | 0.003 |
| Nonionic | 0.4 | 0.8 | 0.8 | 1.2 | 1.2 | 1.2 |
| PEG 6000 | 0.4 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 |
| BTA | 0.04 | 0.04 | 0.04 | - | 0.06 | 0.06 |
| Paraffin | 0.1 | 0.1 | 0.1 | 0.15 | 0.15 | 0.15 |
| Perfume | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 |
| Sulphate | - | - | - | 0.5 | 0.05 | 2.3 |
| <u>Phase 2</u> | | | | | | |
| Ra/Ga-AMG | 0.003 | 0.003 | 0.002 | 0.01 | 0.01 | 0.01 |
| Amylase | 0.0005 | | 0.0004 | 0.0005 | | 0.0004 |
| Protease | 0.009 | 0.008 | 0.01 | 0.009 | 0.008 | 0.01 |
| Citric | 0.3 | | 0.3 | 0.3 | | 0.30 |
| Sulphamic acid | - | 0.3 | - | - | 0.3 | - |
| Bicarbonate | 1.1 | 0.4 | 0.4 | 1.1 | 0.4 | 0.4 |
| Carbonate | - | 0.5 | - | - | 0.5 | - |
| Silicate | - | - | 0.6 | - | - | 0.6 |
| CaCl ₂ | - | 0.07 | - | - | 0.07 | - |
| PEG 3000 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 |

The multi-phase tablet compositions are prepared as follows. The detergent active composition of phase 1 is prepared by admixing the granular and liquid components and is then passed into the die of a conventional rotary press. The press includes a punch suitably shaped for forming the mould. The cross-section of the die is approximately 30x38 mm. The composition is then subjected to a compression force of 940 kg/cm² and the punch is then elevated exposing the first phase of the tablet containing the mould in its upper surface. The detergent active composition of phase 2 is prepared in similar manner and is passed into

the die. The particulate active composition is then subjected to a compression force of 170 kg/cm², the punch is elevated, and the multi-phase tablet ejected from the tablet press. The resulting tablets dissolve or disintegrate in a washing machine as described above within 12 minutes, phase 2 of the tablets dissolving within 5 minutes. The tablets provide excellent dissolution and cleaning characteristics together with good tablet integrity and strength.

Example 22

The following manual dishwashing compositions were prepared according to the present invention :

| | I | II | III | IV | V | VI | VII | VIII |
|--|------|------|------|-----------|-----------|-----------|------|------|
| C12-14E0-3S | 26.0 | 34.2 | 25.0 | 26.0 | 37.0 | 26.0 | 22.0 | 32.0 |
| C11LAS | - | - | - | - | - | - | 13.0 | - |
| C12-14 amine oxide | 2.0 | 4.9 | 2.1 | 6.5 | 5.5 | 6.5 | 1 | - |
| C12-14 betaine | 2.0 | 5.0 | 2.1 | - | - | - | - | 4.0 |
| C12-14 glucose amide | 1.5 | 1.5 | 3.1 | - | - | - | - | - |
| C9-11E8-9 | 4.5 | 1 | 4.1 | 3.0 | 1.0 | 3.0 | - | 1.0 |
| Alkyl Polyglucoside | - | - | - | - | - | - | 12.0 | 3.0 |
| C1-20 Mono Ethanol Amine | - | - | - | - | - | - | 1.5 | - |
| DTPA | - | 0.1 | 0 | 0-500 ppm | 0-500 ppm | 0-500 ppm | 0 | 0 |
| Succinic acid | - | - | - | - | - | 0 | - | 4.5 |
| Cumene sulphonate | - | - | 4.5 | 1 to 6 | - | 1 to 6 | - | - |
| Ca ou Na xylene Sulphonate | - | 5.0 | - | - | 4.0 | - | 2.5 | - |
| Mg salts (in % Mg) | 0.5 | 0.7 | 0.5 | 0.04 | 0.6 | 0.04 | 0.3 | 0 |
| 1,3 bis (methylamino) cyclohexane | - | - | - | 0.5 | - | 0.5 | - | - |
| N,N-dimethylamino ethyl methacrylate homopolymer | - | - | - | 0.2 | - | 0.2 | - | - |
| Citric | - | - | - | 0-3.5 | - | 0-3.5 | - | - |
| Ethanol | 6-8 | 5-8 | 6-9 | 4-10 | 7.0 | 4-10 | 4.0 | 4.0 |
| Protease | - | - | - | 0-0.08 | - | 0-0.08 | - | - |

| | I | II | III | IV | V | VI | VII | VIII |
|--|------------|------|------|--------|-----|--------|-------|------|
| Ra/Ga-AMG | 0.05 | .002 | .005 | 0.01 | 0.4 | 0.05 | 0.002 | 0.01 |
| Amylase | - | - | - | 0.002 | - | 0.005 | 0.04 | 0.05 |
| Carbonate | - | - | - | - | - | 2.5 | - | - |
| Poly Propylene Glycol (MW2000-4000) | - | - | - | 0 to 2 | - | - | - | - |
| pH | 7-8 | 7- 8 | 7-8 | 8.5-11 | 7-8 | 8.5-11 | 7 | 7 |
| Perfume | 0.1-0.7 | | | | | | | |
| Balance (water and minors) | Up to 100% | | | | | | | |

Example 23

The following fabric and hard surface cleaner composition was prepared

5 according to the present invention : '

| | |
|--|------------|
| Sulphate | 18.5 |
| Bicarbonate | 18.6 |
| Polycarboxylate | 4.1 |
| C18 Alpha Olefin | 0.2 |
| Enzyme (lipase, protease and/or cellulase) | 0.004 |
| Amylase | 0.003 |
| Ra/Ga-AMG | 0.05 |
| Brigthener 2 | 0.1 |
| Photoactivated bleach | 0.04 |
| Coated sodium percarbonate | 45.0 |
| TAED | 8.8 |
| Citric | 2.5 |
| Perfume | 0.1 |
| Miscellaneous and water | up to 100% |

WHAT IS CLAIMED IS:

1. A detergent composition comprising a detergent ingredient and a raw starch degrading enzyme characterised by a ratio of activity to degrade raw corn starch (Ra) to activity to degrade gelatinised corn starch (Ga) : [Ra/Ga] above 0.2.
2. A detergent composition according to claim 1 wherein said raw starch degrading enzyme is characterised by a ratio of activity to degrade raw corn starch (Ra) to activity to degrade gelatinised corn starch (Ga) : [Ra/Ga] above 0.35.
3. A detergent composition according to claim 1 wherein said raw starch degrading enzyme is comprised at a level of from about 0.0002% to about 10% pure enzyme by weight of the total detergent composition.
4. A detergent composition according to claim 3 wherein said raw starch degrading enzyme is comprised at a level of from about 0.002% to about 2 % pure enzyme by weight of the total detergent composition.
5. A detergent composition according to claim 4 wherein said raw starch degrading enzyme is comprised at a level of from about 0.002% to about 1% pure enzyme by weight of the total detergent composition.
6. A detergent composition according to claim 1 wherein said raw starch degrading enzyme is selected from the group consisting of an amyloglucosidase EC 3.2.1.3, an α -amylase EC 3.2.1.1, a beta-amylases EC 3.2.1.2, an isoamylase EC 3.2.1.68, a pullulanase type I EC 3.2.1.41, an isopullulanase EC 3.2.1.57, a neopullulanase EC 3.2.1.135, a pullulanase type II, a dextrin dextranase EC 2.4.1.24, a cyclodextrin glycosyltransferase EC 2.4.1.19, a maltogenic alpha-amylase EC 3.2.1.133 and/or mixtures thereof.
7. A detergent composition according to claim 1 wherein said raw starch degrading enzyme has or has been added a starch binding domain.

8. A detergent composition according to claim 1 further comprising an enzyme selected from the group consisting of a lipase, a protease, a conventional α -amylase, a conventional neopullulanase, a conventional pullulanase type I or II and/or mixtures thereof.
9. A detergent composition according to claim 1 wherein said detergent ingredient is selected from the group consisting of nonionic surfactants, flocculating agents, and/or mixtures thereof.
10. Use of raw starch degrading enzyme in a detergent composition for the hydrolysis of raw starch.
11. Use according to claim 9 for the removal of starch-containing stains and soils, and when formulated as laundry compositions, excellent whiteness maintenance and dingy cleaning.

INTERNATIONAL SEARCH REPORT

Inte. Jonal Application No

PCT/US 00/18068

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | EP 0 368 341 A (KAO CORP) 16 May 1990 (1990-05-16) cited in the application claims | 1-6,8-11 |
| A | --- | 7 |
| X | EP 0 450 627 A (KAO CORP) 9 October 1991 (1991-10-09) cited in the application abstract; claims; examples | 1-6,8-11 |
| | -/-- | |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

12 September 2000

Date of mailing of the international search report

20. 09. 2000

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/18068

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | <p>DATABASE WPI Section Ch, Week 199812 Derwent Publications Ltd., London, GB; Class D16, AN 1998-128961 XP002124174 & SE 506 675 C (BARKSTROEM L H), 26 January 1998 (1998-01-26) abstract & SE 9 700 723 A (BARKSTROEM LARS HENRIK) 26 January 1998 (1998-01-26)</p> | 1-5,8-10 |
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/18068

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claim 1 relate to a detergent composition comprising a raw starch degrading enzyme defined by reference to the following parameter :

P1 : ratio of activity to degrade raw corn starch (Ra)
to activity to degrade gelatinised corn starch
(Ga)
: 'Ra/Ga! above 0.2 (pref. above 0.35).

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 84 EPC. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art.

The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to enzymes mentioned in claim 6 and in the description at pages 5-9.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPD policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

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